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Color Removal from Softwood, Kraft, Caustic Extract Effluent by Polyamines

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COLOR REMOVAL FROM SOFTWOOD, KRAFT, CAUSTIC EXTRACT EFFLUENT BY POLYAMINES

A thesis submitted by

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SUMMARY

The objectives of this study were threefold, viz.: (1) to document the scope of the polyamine precipitation of caustic extract color bodies, (2) to determine the extent of polyamine reactivity, and (3) to investigate the role of charge.

The polyamines studied were PEI 18, 12 and 6, branched polymers of polyethylenimine $\underline{M}_n$ 1,800 ± 300, 1,200 ± 150 and 600 ± 100, respectively, tetraethylenepentaamine, triethylenetetraamine, diethylenetriamine, ethylenediamine and its symmetrical N-methyl substituted analogs, 1,3-diaminopropane, 1,4-diaminobutane, 1,12-diaminododecane, and ethylamine. Their effectiveness in the precipitation of color bodies from a reconstituted, freeze-dried, kraft caustic extract effluent (CES) and from a reconstituted, acid precipitated CES color body fraction (Fraction I) was studied at various pH's and polyamine concentrations.

Against CES color, each polyamine had an optimum pH range. For PEI 18, the optimum pH range was from 7 to 8.5; at these pH's, 12 to 18 meqs. of nitrogen/liter produced 85 to 90% color removal. When the PEI 18 concentration was in excess of that required to achieve maximum color reduction, color removal decreased. The lower molecular weight branched polyamines showed a tendency toward a higher pH optimum and lower color removal. The linear polyamines also removed CES color but did it less effectively than PEI 18. The pH optima occurred in acidic conditions and decreased with decreasing polyamine molecular weight, as did the relative rates of precipitation and the maximum color removal. The presence of excess polyamine had little effect on the ultimate color removal. Of the diamines tested, only ethylenediamine and 1,12-diaminododecane were effective in removing CES color.

Fraction I color bodies were far more easily precipitated by all the polyamines, over a wider pH range. Increasing pH increased the solution concentration of polyamine required to achieve maximum color removal and decreased the effect of excess polyamine on color removal by the branched polyamines.

The polyamine contents of several CES and Fraction I color body precipitates were determined directly by total nitrogen analysis and by difference using a spectrophotometric method for supernatant polyamine concentration. The normalized amine content of the precipitates produced by linear polyamines was found to be the same with both color body sources. This was not the case for the branched polyamines, indicating that color removal from CES involved the precipitation of at least two types of color bodies.

At a given pH, the polyamine content of Fraction I precipitates was related to the cationic character of the polyamine. As the pH increased, the precipitate polyamine content increased; polyamine content was also dependent upon the anionic character of the color bodies. Infrared spectroscopy showed that the precipitate retained the ionic character of the reactants, and precipitate counterion analysis showed that overall and localized electrical neutrality was achieved primarily by intimate association of the cationic polyamines with the anionic color bodies. Conductivity and zeta potential measurements were used to probe the mechanism of precipitation, and a general mechanism was proposed; this mechanism involves a rapid initial interaction based on coulombic attraction, which ultimately leads to the formation of larger aggregates that precipitate.

INTRODUCTION

In recent years, water-intensive industries have undertaken programs designed (1) to reduce the amount of raw water required for production and (2) to improve the quality of effluents discharged to the aqueous environment. Many industries, pulp and paper included, routinely provide both primary and secondary treatment for their effluent streams. While treatments such as primary clarifiers and aeration lagoons greatly reduce the amount of suspended solids, biological oxygen demand, chemical oxygen demand and total organic carbon ultimately discharged to the receiving body, they do not remove appreciable amounts of color. Unfortunately, many effluents from the pulp and paper industry are highly colored and thus lower the aesthetic quality of the receiving body and reduce the depth of light penetration, thus promoting biological unbalance. For these reasons and in anticipation of future legislation, the pulp and paper industry has recently emphasized the investigation of various methods for the removal of color from their effluent streams.

The most highly colored effluents from pulp and paper mills originate in the bleaching process. In bleaching, the pulp is first chlorinated, and then it is washed, concentrated, and extracted with caustic. This caustic extract is highly colored, and it has been estimated that 60 to 70% of the total color discharged from bleached kraft mills is derived from the caustic extract (1). Thus, it is not surprising that caustic extracts have received special attention in attempts to evaluate methods and mechanisms of color removal.

Typically, caustic extracts are fairly dilute, containing between 0.1 and 1.0% dissolved solids*. Of this, approximately one-half to two-thirds is found to be fixed solids, predominantly sodium chloride, with the remainder attributed to degradation products of lignin, carbohydrates, and possibly extractives from the chlorinated pulp.

A few years ago most workers would have agreed that lignin degradation products were almost completely responsible for caustic extract color (2). However, Collins, et al. (3) has recently suggested that carbohydrate degradation may contribute more to caustic extract color than had been previously assumed. While specific chromophores have yet to be identified, a number of investigators have speculated that quinones and unsaturated cyclic carbonyl-containing moieties may be the most important (4-7).

The polydisperse nature of caustic extract has discouraged attempts at extensive characterization, but a few people have tried to elucidate the general structure of caustic extract components. Perhaps the most extensive study was that by Dence, et al. (8) and Bennett, et al. (9). They concluded that organic materials in caustic extract were low molecular weight (< 500), chlorine substituted, acidic compounds which displayed little or no aromatic character. They attributed 70 to 80% of the total acidity to carboxylic acids and concluded that enolic and, to a lesser extent, phenolic hydroxyls were responsible for the remainder of the acidity.

When Collins, et al. investigated caustic extract, they too observed little ligninlike character (10). However, the colored components appeared

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* Using the U.S. Public Health Service nomenclature, dissolved solids are those residues which pass through a 5 μm filter and are not volatilized at 103°C. Fixed solids are the portion of the dissolved solids which remains after heating at 550°C.

to be quite polydisperse and some fractions had apparent molecular weights which were over 10,000. Dugal, et al. (11) investigated caustic extract color bodies and his results generally agreed with those of Collins, et al. (10) except that he observed apparent molecular weights as high as 125,000 for some fractions.

A variety of methods for color removal have been investigated. These include precipitation by di- and trivalent metal cations (12,13), ion exchange (14), extraction using emulsified long-chain aliphatic amines in hydrocarbon solvents (15), adsorption by activated carbon (16) or synthetic resins (17), reverse osmosis (18), and oxidative methods, both chemical (19) and photochemical (20). None of these methods has provided a totally acceptable solution to the color problem.

The most thoroughly investigated color removal procedures are those utilizing lime (calcium oxide). Full-scale field installations have shown that the addition of 20,000 ppm of lime to caustic extract reduces color by 85-90% (21). This system is known as "massive lime treatment." A modification of this procedure known as "stoichiometric lime" or "minilime" uses lime concentrations of 1,000 to 2,000 ppm. In the latter system color removal is somewhat lower, and sludge handling is more of a problem (22).

The mechanism of color removal by lime precipitation was studied by Dence, et al. (8) and Bennett (9). They concluded that the precipitation was a chemical rather than physical phenomenon, resulting from the interaction of calcium ion with the very weakly acidic groups, enolic and phenolic hydroxyls, to form insoluble calcium salts. Failure to obtain complete color removal was attributed to the presence of comparatively low molecular weight substances, <250, whose calcium salts were soluble under their testing conditions.

In a later work, Dugal, et al. (11) showed that caustic extract color bodies which had been separated on the basis of acid solubility were also selectively precipitated on the basis of molecular weight. Those color bodies soluble at pH 1 had molecular weights ranging from 100 to 1,100, whereas those color bodies insoluble at pH 1 had molecular weights ranging from 100 to as high as 125,000.

PRESENTATION OF THE PROBLEM

In the previous section, it was pointed out that the generally accepted mechanism of color removal by lime is based on the insolubility of calcium salts, particularly calcium enolate salts (9). With this interpretation in mind, it was considered somewhat surprising to find that simple polyamines such as diethylenetriamine were effective in removing caustic extract color (23). The reaction was rapid and was dependent upon the pH of the medium. At optimum conditions, a dense nonhydrous precipitate settled rapidly, compacted to < 5% of the sample volume within hours, and was insoluble at neutral or acidic pH's (23). Since these properties would allow easy dewatering, it was thought that the precipitation of caustic extract color bodies by polyamines warranted further investigation.

Since the reaction was pH dependent, it was hypothesized that the precipitation proceeded via charge interactions between the cationic ammonium salts of the polyamine and the anionic color bodies. The objectives of the thesis were to document the scope of the phenomenon, to determine the extent of polyamine reactivity, and to investigate the role of charge.

GENERAL APPROACH

The general approach to the problem was to study the effects of a series of ethylenimine polymers and low molecular weight polyamines, at various pH's and polyamine concentrations, on the color bodies contained in a commercially produced, partially characterized caustic extract effluent.

The polyamines selected for study were such that the data obtained in the initial survey portion of the study would also apply to investigation on the role of charge.

RESULTS AND DISCUSSION

COLOR REMOVAL FROM CAUSTIC EXTRACT EFFLUENTS

In the Introduction, reference was made to some personal observations which indicated that polyamines could precipitate the color bodies present in a sample of caustic extract. It was conceivable that these observations were made under a unique set of circumstances and that they might not be reproduced when other caustic extract effluents were used. To test this, several different caustic extract effluents were treated with PEI 18* at pH 7; the results are shown in Table I.

TABLE I

COLOR REMOVAL FROM CAUSTIC EXTRACT EFFLUENTS BY PEI 18 AT pH 7

Mill	Fiber Source	Initial Absorbance, 450 nm	Maximum Color Removal, %	PEI Concentration Required, ppm
A	Mixed softwood	3.2	89	600
B	Mixed softwood	4.0	96	400
C	ca. 95% Softwood, 5% hardwood	4.6	95	800
D	70% Softwood, 30% hardwood	3.1	92	200

Although good color removal was obtained in each case, there was some variation in the polyamine concentration required to achieve maximum color removal. These data showed that the precipitation of caustic extract color bodies by polyamines is a general phenomenon and that there will be variations in the effectiveness of polyamines from mill to mill. Rather then survey the

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*A branched polymer of ethylenimine, $\underline{M}_n$ 1,800 ± 300.

effects of polyamines on effluents from several different mills, I chose to focus on the effects of various polyamines on the color present in a single caustic extract effluent. For this, a sample of softwood, kraft caustic extract effluent was obtained from a nearby mill (Mill A).

In most previous studies of color removal from caustic extract, the investigators stored the effluents at temperatures near zero degrees centigrade and withdrew samples as needed (3,8). Such treatment would be suitable for relatively unreactive caustic extract components that do not change at all or change insignificantly during storage. More recently, Dugal, et al. (11) chose to freeze-dry a sample of effluent and reconstitute the color bodies just prior to use. They showed that freeze-drying had no apparent effect on effluent color or sedimentation coefficient even with long periods of storage. Since it was thought that the period of experimentation in the present study would be lengthy in comparison to some of the others reported, it was decided that a freeze-dried caustic extract sample would be the preferred source of color bodies. To this end, Mill A caustic extract was filtered and freeze-dried. Then the effluents as received and after freeze-drying and reconstitution were partially characterized in an effort to determine whether any significant changes had occurred during processing.

CHARACTERIZATION OF MILL A CAUSTIC EXTRACT

Table II shows a partial characterization of Mill A caustic extract, as received and after freeze-drying and reconstitution.

With the exception of pH, BOD_5, and sodium ion content, the values of the various parameters determined before and after freeze-drying and reconstitution were essentially the same.

TABLE II

CHARACTERIZATION OF MILL A CAUSTIC EXTRACT

Parameter	As Received	After Freeze-Drying and Reconstitution
Suspended solids (ppm, 103°C)	11.1	0
Dissolved solids (ppm, 103°C)	8530	8470
Total solids (ppm, 103°C)	8541	8470
Fixed solids (ppm, 550°C)	3664	3656
Turbidity (t.u.)	<1	<1
Sedimentation coefficient (S_w^{20})	1.21	1.21
Specific conductivity (mhos/cm)	6.22×10^{-2}	6.19×10^{-2}
Calcium (ppm)	72	47
Total alkalinity (ppm as $CaCO_3$)	507	461
TOC (ppm)	2575	2450
TIC (ppm)	125	112
BOD_5 (ppm)	958	672
Initial pH	9.15	9.58
Sodium (ppm)	855	1190
Chloride (ppm)	1048	1048
Sulfur (ppm)	143	140
Nitrogen (ppm)	a	88
Trace metals (ppm)	a	19.77
Aluminum		0.35
Barium		0.47
Copper		0.15
Iron		2.80
Magnesium		0.90
Manganese		0.10
Silicon		15.0
Total sugars (ppm)[b]	a	71
Araban		4
Galactan		35
Glucan		15
Mannan		3
Xylan		14

[a] Not determined.

[b] After hydrolysis, as anhydro aldose.

The slightly higher initial pH of the freeze-dried sample could be attributed to the loss of weakly acidic volatile organic material. Such a loss, combined with the loss of volatile organics, could also explain the lower BOD_5 observed. The difference in the sodium ion contents is probably within the precision of the method (24).

The data in Table II show that Mill A caustic extract contained some carbohydrate. While this observation is contrary to the results reported by Dence, et al. (8), it is in agreement with the results obtained by both Dugal, et al. (11) and Collins, et al. (3). This is another indication that caustic extract components will vary from mill to mill.

The titration of Mill A caustic extract as received and after freeze-drying and reconstitution is shown in Fig. 1. The freeze-dried material had a higher initial pH; however, after the samples were acidified and vacuum degassed to remove CO_2, back titration with sodium hydroxide showed no significant differences.

Figure 2 shows the absorption spectra of Mill A caustic extract, as received and after freeze-drying and reconstitution at pH 9.5. The spectra are essentially identical.

Thus the data from the partial characterization verify Dugal's, et al. finding, that freeze-drying has little significant effect on the general character of caustic extract color bodies and suggests that the freeze-dried material can be used as a caustic extract standard (CES).

The effects of changing pH on the absorption spectrum of CES are shown in Fig. 3. Decreasing pH decreased the absorption at all wavelengths tested, implying that various weakly acidic groups serve as chromophores or auxochromes

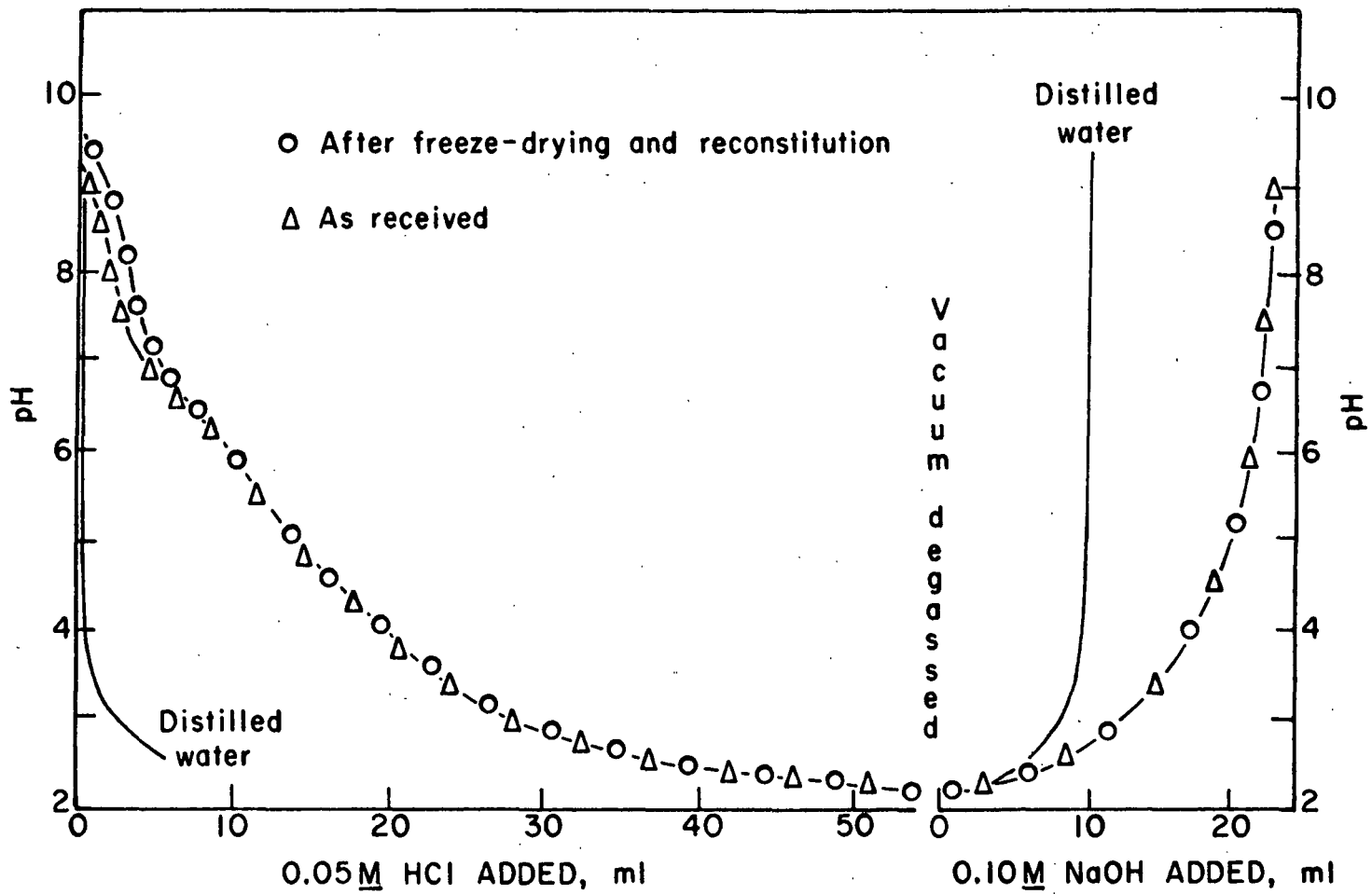

Figure 1. The Titration of Mill A Caustic Extract, as Received and After Freeze-Drying and Reconstitution. (In Each Case 50.0 ml of Sample was Diluted with 50.0 ml of Distilled Water Prior to Titration.)

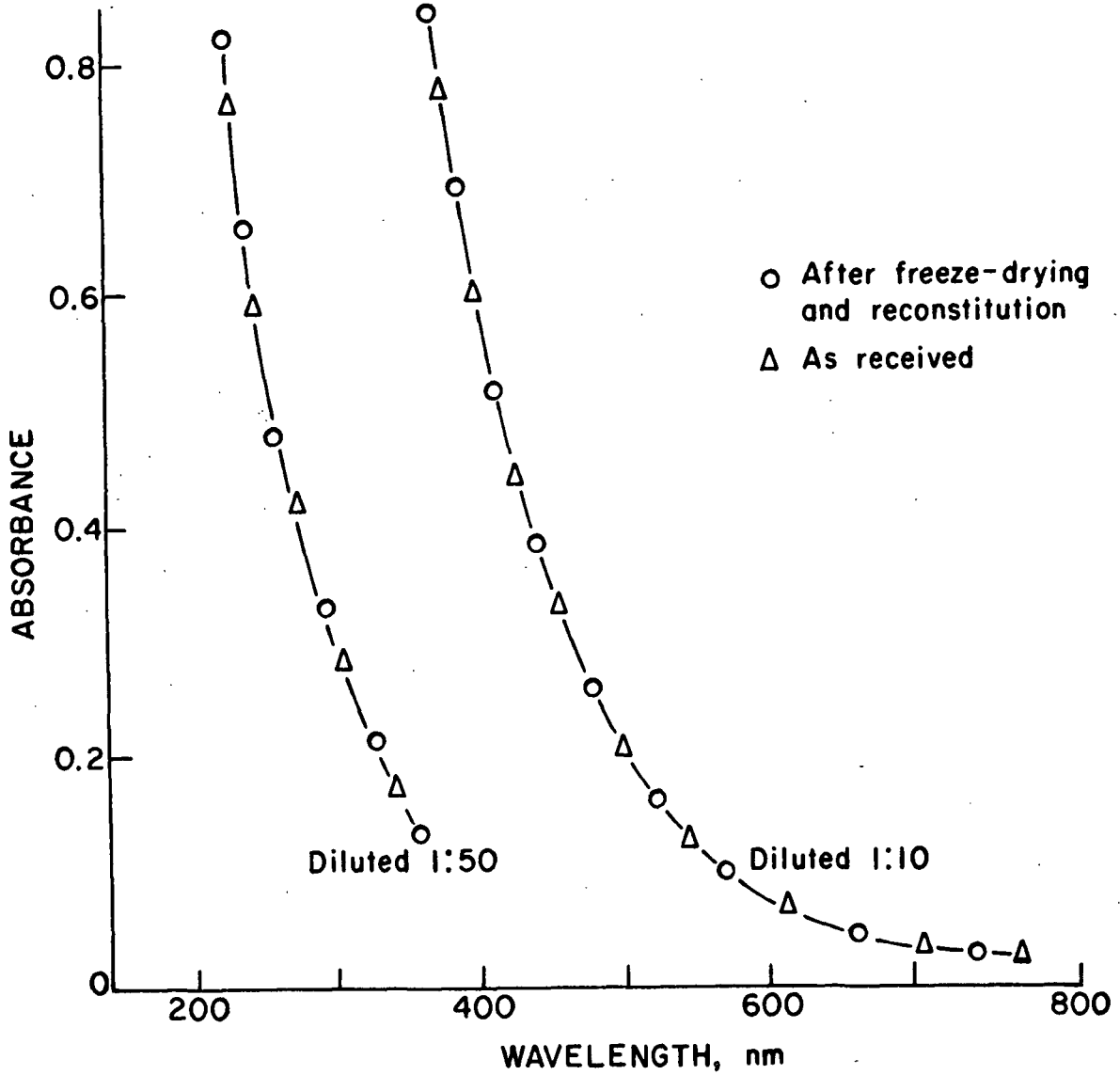

Figure 2. The Absorption Spectrum of Mill A Caustic Extract, as Received and After Freeze-Drying and Reconstitution

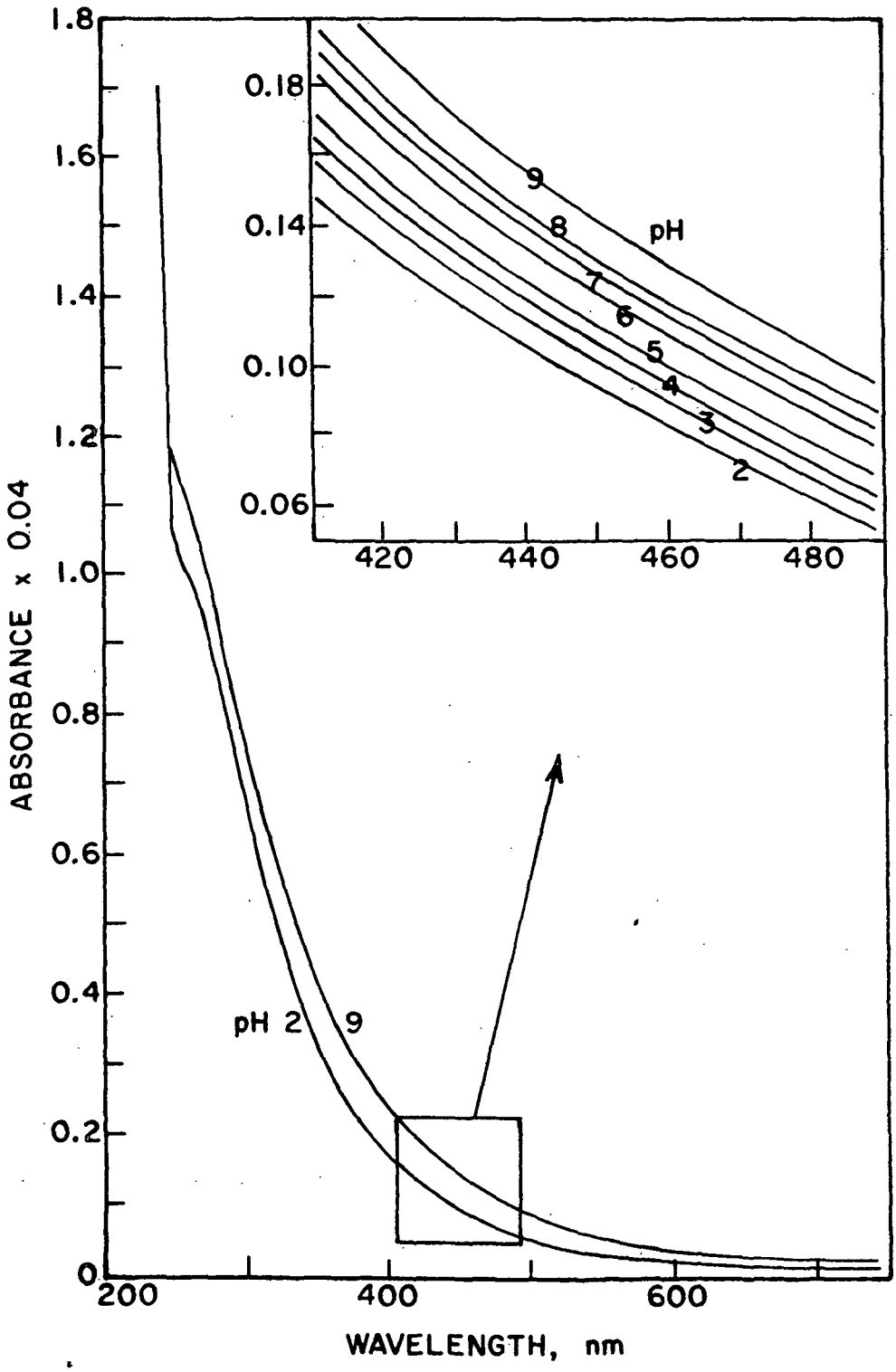

Figure 3. The Absorption Spectra of CES at Several pH's

when ionized. Since no isosbestic point was observed, it was decided that the reference wavelength in the forthcoming color removal experiments would be 450 nm. The choice was arbitrary; had the program been initiated at a later date, the reference wavelength would have been 465 nm, in accord with the recently adopted standard method for color measurement (25).

COLOR REMOVAL FROM CES

After it was concluded that CES would provide a satisfactory source of caustic extract color bodies, the next step in the program was to test various amines for color removing ability. The color removal assay was as follows: A sample of CES was reconstituted at the desired pH and then the volume was adjusted to one-half that required to return CES to its original concentration. Then, in order, water and polyamine solutions at the desired pH were added to an aliquot of CES with mixing. In all cases the final reaction volume was such that CES was restored to its original concentration, 0.91 g/100 ml. The vessels were capped, stored in the dark at 20°C for 24 ± 1 hour, and then centrifuged. The supernatant solutions were decanted and their optical densities at 450 nm were determined and expressed as the percent of the original optical density remaining and plotted versus the polyamine concentration expressed in meqs of nitrogen per liter (meq N/liter).

COLOR REMOVAL BY BRANCHED POLYAMINES

Figure 4 shows the color removal curves for the branched polyamines* studied, at several pH's and polyamine concentrations. The largest polyamine

*Branched polyamines studied were PEI 18, 12 and 6. These are polymers of ethylenimine, M_n 1,800 ± 300, 1,200 ± 150 and 600 ± 100, respectively. See Appendix I for structures.

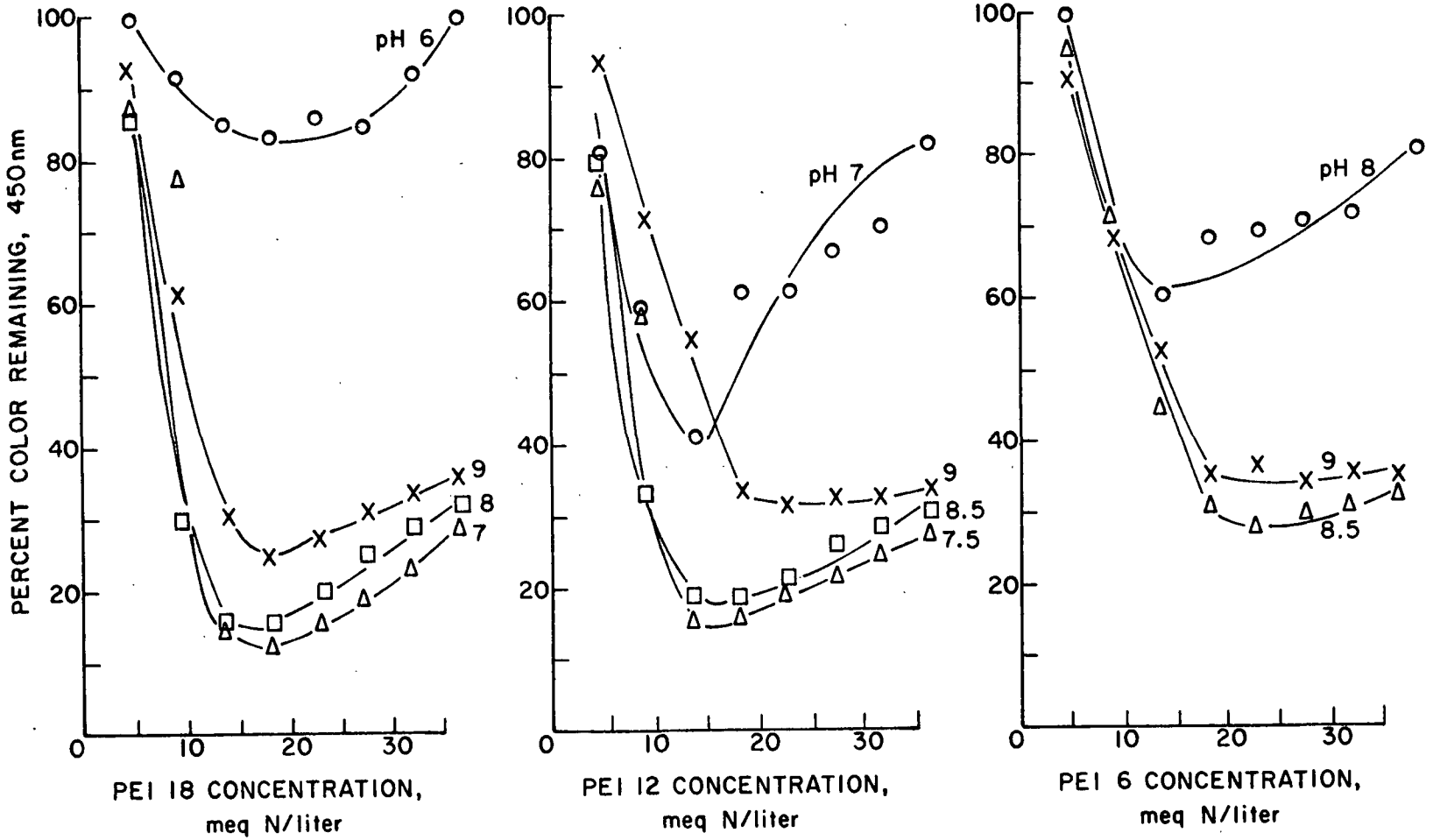

Figure 4. Color Removal from CES — the PEI Series

studied, PEI 18, was the most effective precipitant, achieving 85-90% color removal at pH's between 7 and 8.5 and polyamine concentrations of 12 to 18 meqs of nitrogen per liter. Under these conditions the addition of PEI 18 caused an instantaneous turbidity, followed closely by the appearance of a dense precipitate which settled rapidly.

The precipitation was dependent upon both the pH of the medium and the polyamine concentration. When the pH was 6 or 9, color removal was less effective. When PEI 18 concentrations were in excess of that required to achieve maximum color removal, the precipitation was less effective; only 40% color removal was observed at PEI 18 concentrations of ca. 64 meq N/liter at pH 7.5 (see Table III). These conditions produced a precipitate which settled slowly.

Color removal by PEI 12 was much the same as that observed for PEI 18, except that the pH optimum occurred at slightly more alkaline pH's, pH's 7.5 to 8.5, and the effects of excess polyamine were less noticeable (see Table III).

When PEI 6 was the precipitant, maximum color removal decreased to about 65%, the pH optimum increased to between 8.5 and 9.0, and color removal appeared to be far less sensitive to the presence of excess polyamine.

COLOR REMOVAL BY LINEAR POLYAMINES

In the next phase of the investigation the effects of linear polyamines on CES color bodies were determined; the results are shown in Fig. 5. These also precipitated CES color bodies but did so less effectively than PEI 18 or 12. The relative rates of precipitation, as judged by the onset of turbidity and ultimate color removal, decreased with decreasing polyamine molecular weight.

TABLE III

CES COLOR REMOVAL AND PRECIPITATE DRY WEIGHTS
FROM POLYAMINES AT OPTIMUM pH's

Polyamine, ppm	Concentration, meq N/liter	% Color Removal[a]	Precipitate Dry Weight, mg	Ratio, % color removal[a]/ precipitate dry weight[b]
PEI 18 (pH 7.5)				
400	9.1	84.6	19.3	4.36
600	13.7	85.6	22.9	3.73
800	18.2	79.6	22.3	3.57
1000	22.7	73.7	22.7	3.25
1600	36.3	61.4	21.5	2.85
2200	50.0	49.5	19.0	2.61
2800	63.5	37.4	17.0	2.20
PEI 12 (pH 8.0)				
400	9.1	64.8	14.2	4.75
600	13.7	84.6	22.2	3.81
800	18.2	81.5	21.9	3.72
1000	22.7	78.1	22.3	3.50
1600	36.3	69.4	22.3	3.11
2200	50.0	61.9	20.6	3.00
2800	63.5	55.4	20.5	2.70
PEI 6 (pH 8.7)				
600	13.7	60.8	12.6	4.83
800	18.2	63.8	15.0	4.25
1000	22.7	64.0	16.0	4.00
1600	36.3	62.1	16.8	3.70
2200	50.0	60.3	16.2	3.72
2800	63.5	55.4	15.4	3.68
Tetraethylenepentaamine (pH 5.0)				
400	10.5	52.0	11.0	4.73
600	15.7	67.3	13.6	4.94
800	21.1	68.5	14.9	4.60
1000	26.4	69.6	14.3	4.85
1600	42.3	70.3	14.0	5.05
2200	58.2	69.2	13.6	5.10
2800	74.0	70.9	14.9	4.76
Triethylenetetraamine (pH 4.0)				
400	10.9	51.0	9.9	5.15
600	16.4	57.2	11.4	5.02
800	21.9	59.7	12.5	4.76
1000	27.4	60.3	12.7	4.75
1600	43.9	61.5	13.7	4.49
2200	60.4	60.1	12.7	4.73
2800	76.6	58.8	12.7	4.63
Diethylenetriamine (pH 4.0)				
400	11.6	35.7	7.3	4.89
600	17.4	48.0	9.5	5.05
800	23.3	49.5	10.3	4.81
1000	29.1	52.8	11.7	4.51
1600	46.6	56.1	12.0	4.68
2800	81.5	55.0	12.1	4.55

[a] Percent of 450 nm absorbance removed.

[b] Equivalent to an initial volume of 10.0 ml.

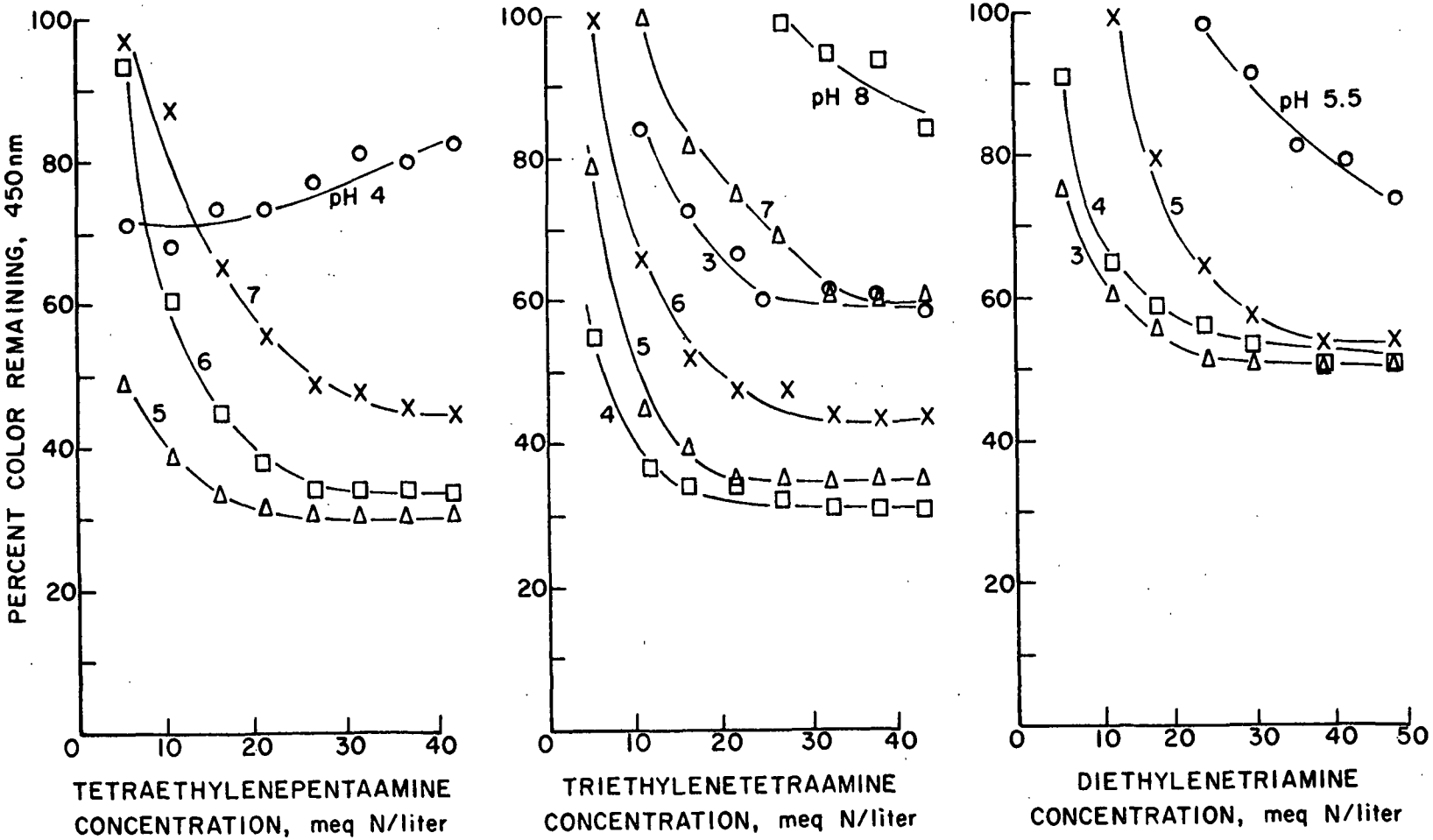

Figure 5. Color Removal from CES — the Ethylenimine Oligomer Series

Figure 5A shows color removal by tetraethylenepentaamine at various pH's and polyamine concentrations. The maximum color removal was about 70%, which occurred between pH's 5 and 6 with polyamine concentrations of 16 meq N/liter or more. As before, the precipitation was dependent upon the pH of the precipitation medium but, in contrast to what was observed with the PEI series, the presence of excess polyamine had little effect on the ultimate color removal levels except at pH 4. Tetraethylenepentaamine concentrations as high as 64 meq N/liter still removed 70% of the color at pH 5 (see Table III).

Color removal by triethylenetetraamine is shown in Fig. 5B. The color removal levels were about the same as for tetraethylenepentaamine. However, the pH optimum occurred at slightly more acidic conditions, pH's 4 to 5. Again, color removal was dependent on the pH of the precipitation medium; when the pH was 3 or 6 color removal was less effective. Excess polyamine had little effect on the color removal observed.

Figure 5C shows color removal by diethylenetriamine. This triamine achieved a maximum color removal of only about 50% at pH's between 3 and 4 and was a poorer precipitant than the other linear polyamines in that almost all of the precipitate was suspended in the medium, even after 24 hours of standing.

COLOR REMOVAL FROM CES BY MONO- AND DIAMINES

Ethylenediamine, N,N'-dimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine, hexamethylethylenediammonium diiodide, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane and ethylamine were all tested for color removing ability. Of these, only ethylenediamine was found to be effective, achieving a maximum color removal of only 20% at pH's between 3 and 4 and concentrations in excess of 0.1M or 200 meq N/liter (Fig. 6).

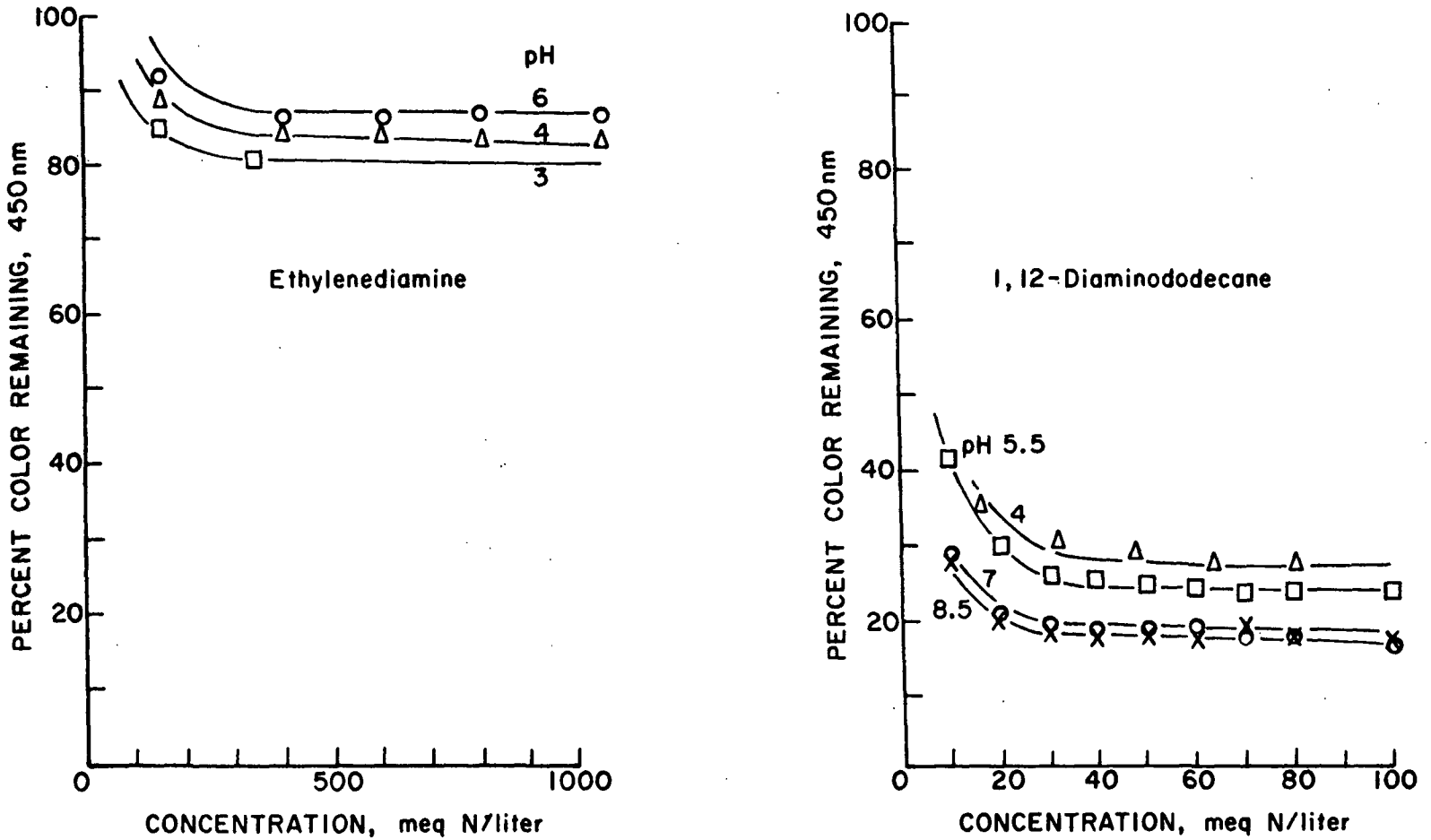

Figure 6. Color Removal from CES by Ethylenediamine and 1,12-Diaminododecane

Under these conditions the reaction medium was hazy, and no settled precipitate could be observed without centrifugation.

In light of these observations, it was somewhat surprising to find that 1,12-diaminododecane was quite effective in removing CES color (Fig. 6). Color removal was different from that previously observed in that 1,12-diaminododecane was effective over a wide pH range, from 8.5 to 4, and contrary to the trends established with the other linear polyamines, color removal was most effective at alkaline pH's.

It is quite possible that the enhanced color removal observed in the case of 1,12-diaminododecane is due, in part, to differences in the polyamine-solvent (water) interactions, resulting from the presence of the twelve carbon chain. This hypothesis is supported by the fact that 1,12-diaminododecane is a waxy solid and appreciably soluble in water only when diprotonated. The other amines tested were miscible with water at all pH's.

For these reasons and in view of the fact that it has been shown that polyanions can be effectively precipitated by long-chain aliphatic ammonium salts (20,26), it was hypothesized that the precipitation of CES color bodies by 1,12-diaminododecane was different from the precipitation by the other polyamines mentioned; while 1,12-diaminododecane will be mentioned in the future, no attempt will be made to correlate its effects with the effects of the ethylenimine-related polyamines.

PRECIPITATE DRY WEIGHTS

The preceding discussion has shown that each polyamine had a color removal pH optimum, i.e., a limited pH range wherein maximum color removal was observed. The dry weights of precipitates obtained within the optimum pH range of several polyamines are shown in Table III.

PEI 18 did not promote color removal. Color removal decreased from 86 to 38% as the PEI concentration was increased from 14 to 64 meq N/liter. Precipitate dry weight also decreased; however, the decrease was not proportional to the decrease in color removal. This lack of proportionality is reflected in the color removal/precipitate dry weight ratios given in the far right column. These data show that the composition of the precipitate changed as the PEI 18 concentration was increased. As will be shown later (p. 53) the change occurred without a significant change in the PEI content of the precipitate, indicating that the color bodies initially precipitated were replaced by other, less chromophoric CES components. The same trend was noticed with both PEI 12 and 6, but the magnitude of the changes became progressively less.

In contrast to the observed effects of excess PEI on precipitate dry weight, when the linear polyamines were the precipitants, the ratio of percent color removal to precipitate dry weight remained fairly constant, suggesting constant precipitate composition. Furthermore, the color removal/precipitate dry weight ratios for the three linear polyamines are very nearly the same, implying that the precipitate compositions may be quite similar.

POLYAMINE PROTONATION AS A FUNCTION OF pH

The previous observations that color removal was dependent upon the pH of the precipitation medium suggested that the ionic character of the interacting species is of some importance in the precipitation. More specifically, the ionic character of the polyamines was of primary importance, since the color bodies appeared to play a passive role, i.e., merely responding to polyamines at certain pH's. Before I relate the ionic character of the

amines to optimum color removal, I want to briefly review the theoretical changes in amine ionic character as a function of pH and the experimentally determined values for the amines used in this work.

Simple amines are weak bases in the Bronsted sense because they accept protons, leaving the reaction medium enriched with hydroxide ions.

$$R_1R_2R_3N: + H^+ + OH^- \rightleftharpoons R_1R_2R_3\overset{+}{N}H + OH^- \qquad (1)$$

When the R groups are hydrogen, the amine is ammonia and the conjugate acid has a pK_a of 9.2. When one of the R groups is alkyl, inductive effects increase the relative basicity, and the pK_a of the conjugate acid increases to about 10.6. The addition of a second alkyl group again increases the pKa but only slightly in comparison to the effects of the first. A third alkyl substitution can actually lower the pK_a, as in the case of trimethylamine which has a pK_a of 9.8 *versus* 10.8 for dimethylamine. This effect has been attributed to a decrease in solvent (water) affinity (27). Tetraalkylation, to give a quaternary salt, ties up the previously free electron pair, and consequently protons can no longer be accommodated. In general, when dissolved in water, tetraalkylammonium salts are considered to be completely ionized (27).

When a single molecule possesses two amino groups, the pK_a of the first is generally >10. The pK_a of the second is strongly influenced by coulombic effects from the initial ionization. Table IV shows that as the distance between the existing and the potential cationic site decreases, increasing the electrostatic repulsive forces, the pK_a of the second amino group becomes further removed from that of the first.

TABLE IV

THE pK_a's OF SEVERAL DIAMINES[a]

	pK_a (1)	pK_a (2)
Ethylenediamine	10.0	7.0
1,3-Diaminopropane	10.1	8.6
1,4-Diaminobutane	10.8	9.4
1,8-Diaminooctane	11.0	10.1

[a] From Albert and Serjeant's Ionization constants of acids and bases (27).

Similarly, the individual pK_a's of tri- and polyamines would be influenced primarily by the structure of the polyamine; however the ionic character at a given pH can also be affected by other factors such as counterion concentration (28,29).

The ionic character of the amines of interest as a function of pH was determined by titrating the free amine with dilute hydrochloric acid. These data are shown in Fig. 7 and 8* and are, for the most part, what one would have expected based on the previous discussion. It may be of interest to note the disappearance of distinct pK's as the number of amino groups per molecule increases. This can be done by comparing the shape of the ethylenediamine titration curve with the curve for tetraethylenepentaamine in Fig. 7.

* During characterization as described in Table II, CES was shown to contain ca. 2,000 ppm NaCl. The inclusion of this amount of NaCl in the titration medium had little effect on the titration profiles observed.

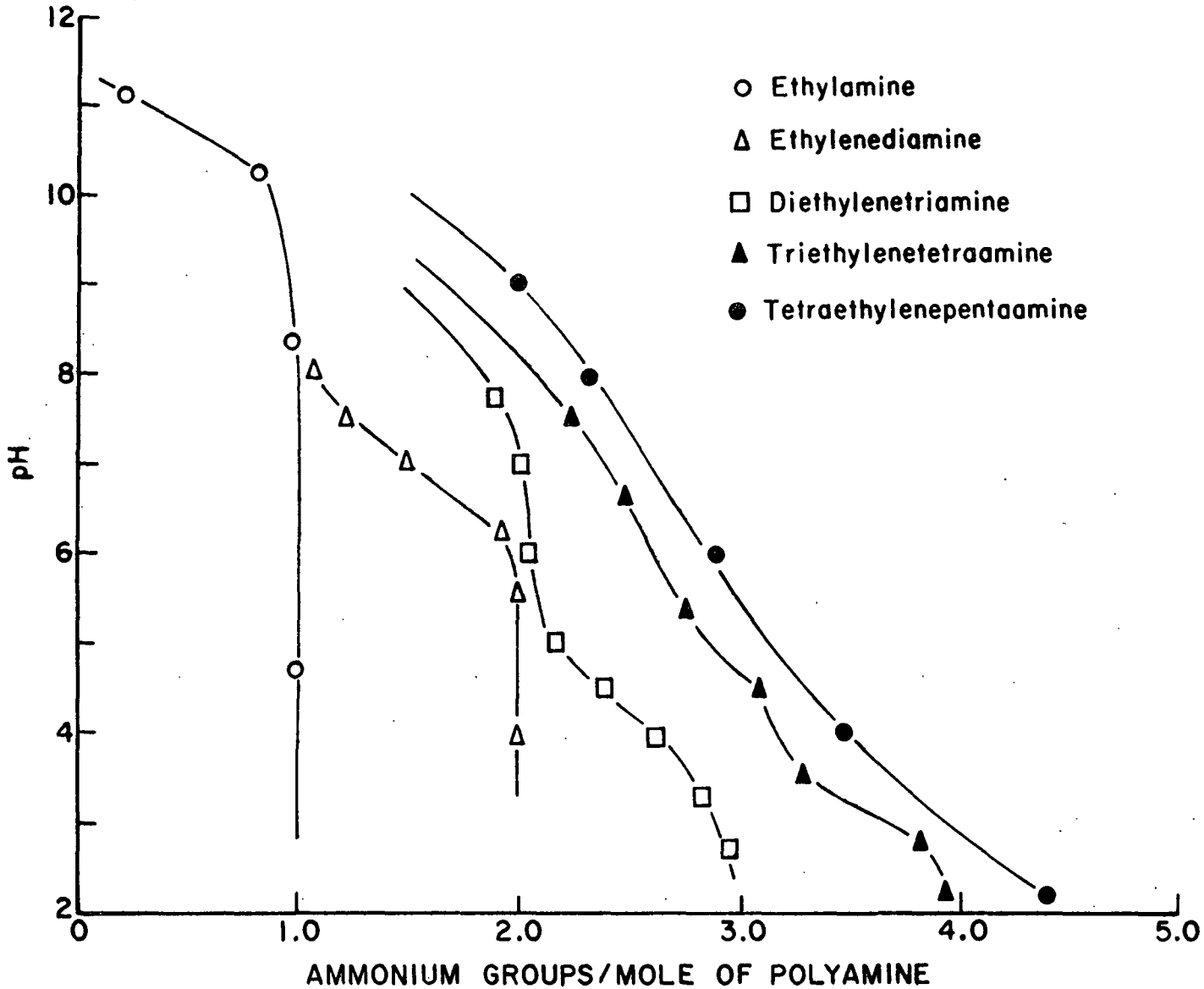

Figure 7. Polyamine Protonation as a Function of pH

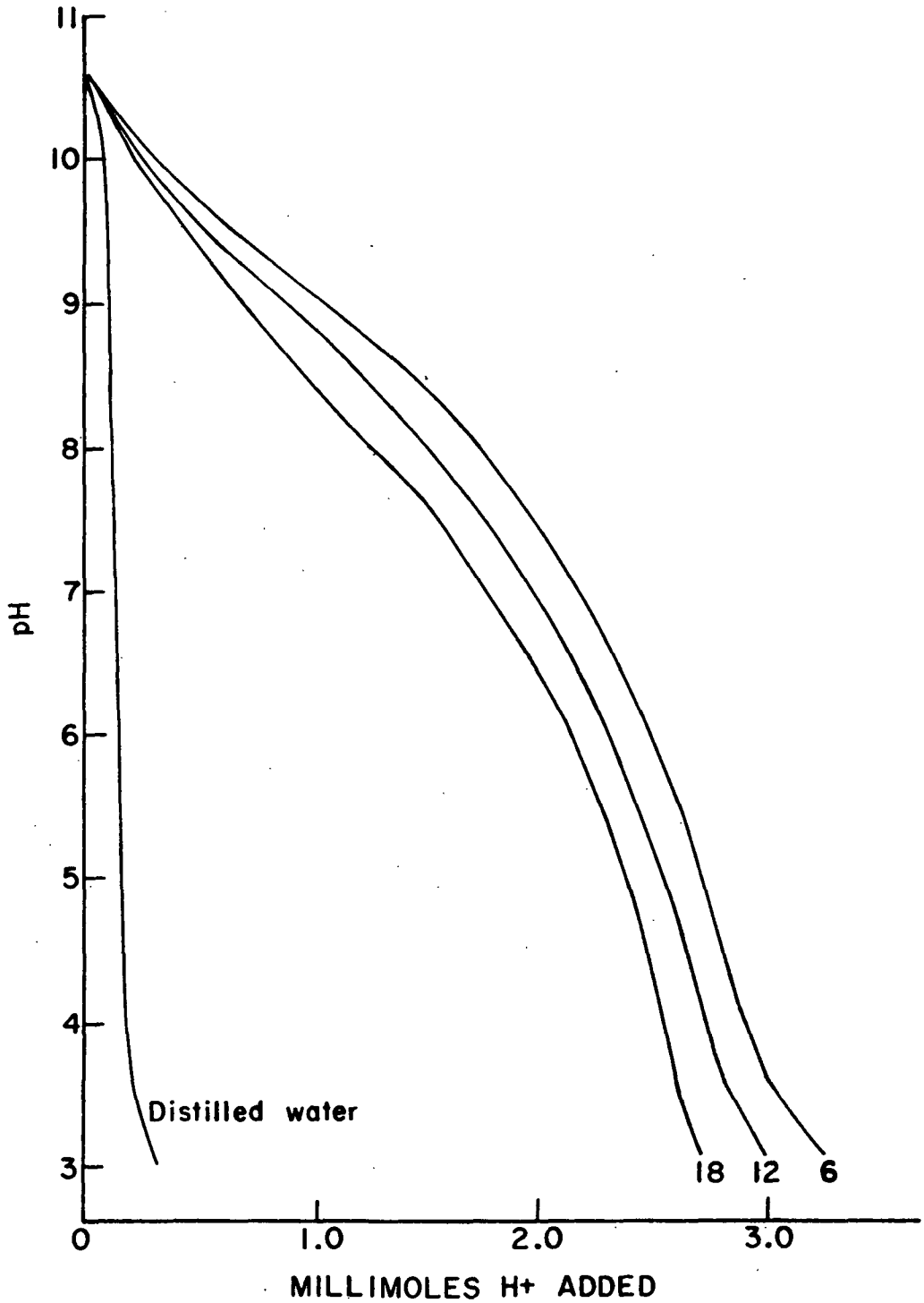

Figure 8. The Titration of PEI 18, 12, and 6 with Hydrochloric Acid (at 36 meq N/200 ml, in 2,000 ppm Sodium Chloride)

POLYAMINE PROTONATION AT OPTIMAL COLOR REMOVAL

The data used in construct Fig. 7 and 8 wereused to estimate the percent protonation for several of the polyamines at the pH's corresponding to maximum color removal. The values obtained are shown in Table V.

TABLE V

POLYAMINE PROTONATION AT OPTIMUM COLOR REMOVAL

Polyamine	Maximum Color Removed, %	Optimum pH	Protonated Sites per Molecule at Optimum pH, %
Ethylenediamine	20	4-3	2.0 (100)
Diethylene-triamine	50	4-3	2.6-2.9 (86-97)
Triethylene-tetraamine	70	5-4	2.7-3.3 (66-83)
Tetraethylene-pentaamine	70	6-5	2.9-3.2 (58-64)
PEI 6	75	9.0-8.5	4.6-6.1 (33-44)
PEI 12	85	8.5-7.5	10.5-14.7 (35-49)
PEI 18	89	8.5-7.0	13.8-20.5 (33-50)

For di- and triamines the pH optima occurred when completely, or nearly completely, protonated species were present. When triethylenetetraamine was the precipitant, color removal was at a maximum at about 75% protonation, i.e., three cationic sites per molecule. Tetraethylenepentaamine achieved maximum color removal at ca. 60% protonation which also corresponds to three cationic sites per molecule.

These data showed that color removal by the linear polyamines could be related to the ionic character of the polyamines. The relationship established was that color removal can be achieved when there are two or more cationic

sites per molecule; however precipitation was more effective when three cationic sites were present. When the number of amino groups per molecule exceeds three, color removal was favored by increasing charge separation.

Table V also shows percent protonation associated with maximum color removal by the branched polyamines. Although the pH optima varied within the series, maximum color removal occurred at similar degrees of protonation, 35 to 50%. This percentage followed the trend established earlier with the linear polyamines, namely that color removal was favored when there was some charge separation.

THE ACID FRACTIONATION OF CES

The data presented up to this point seemed to indicate that color removal was dependent upon both the molecular weight and ionic character of the polyamine. However, very little could be said about the role of the color bodies. They appeared to be passive, merely responding to polyamine concentration and ionic character. The problem was further complicated by the fact that only a portion of the CES components were precipitated. It was thought that some of the difficulty could be alleviated by using a color body system which had a lower proportion of nonprecipitable material. Dugal, et al. (11) had shown that caustic extract color bodies could be fractionated on the basis of their solubility at acid pH's. The acid-insoluble material he obtained was of higher molecular weight, more chromophoric, less acidic, and more easily precipitated by lime than the acid-soluble material. This fractionation technique seemed to present a method for obtaining a color body fraction which could be used to obtain a clearer view of the factors influencing the precipitation of caustic extract color bodies by polyamines. To this end, a concentrated solution of CES was acidified to pH 1 and

allowed to stand overnight at 4°C. During this period a precipitate formed. It was collected by centrifugation, slurried with distilled water and freeze-dried.

The freeze-dried, acid-insoluble CES color body fraction, herein referred to as Fraction I, represented about 10% of the initial CES weight but contained 40% of the initial 450 nm absorbance. Fraction I was only partially soluble in distilled water but was readily resolubilized when the pH was adjusted to 7 or above.

The absorption spectra of Fraction I, the acid-soluble fraction (Fraction II), Fractions I and II recombined, and CES, all at pH 7.5, are shown in Fig. 9. When Fractions I and II were recombined, the absorption spectrum could not be distinguished from that of CES, suggesting that no significant changes in chromophores or auxochromes had occurred during the acidification.

A preliminary titration of Fraction I indicated that it contained about 6% of the total CES acidity (Fig. 10). Since it represented 10% of the weight, this means it was only 60% as acidic as CES on a weight basis. Figure 11 shows a second titration using more dilute titrant and a more concentrated solution of Fraction I. The forward (sodium hydroxide added) and back (hydrochloric acid added) titration curves were not superimposable at pH's below 7. This can be attributed, most likely, to the fact that in the initial titration with base, Fraction I was not completely resolubilized until pH 7 or so; prior to this the solution was hazy. In the back titration, this was not the case. Fraction I was soluble and the solution remained clear down to about pH 2.5 where a slight haziness did develop.

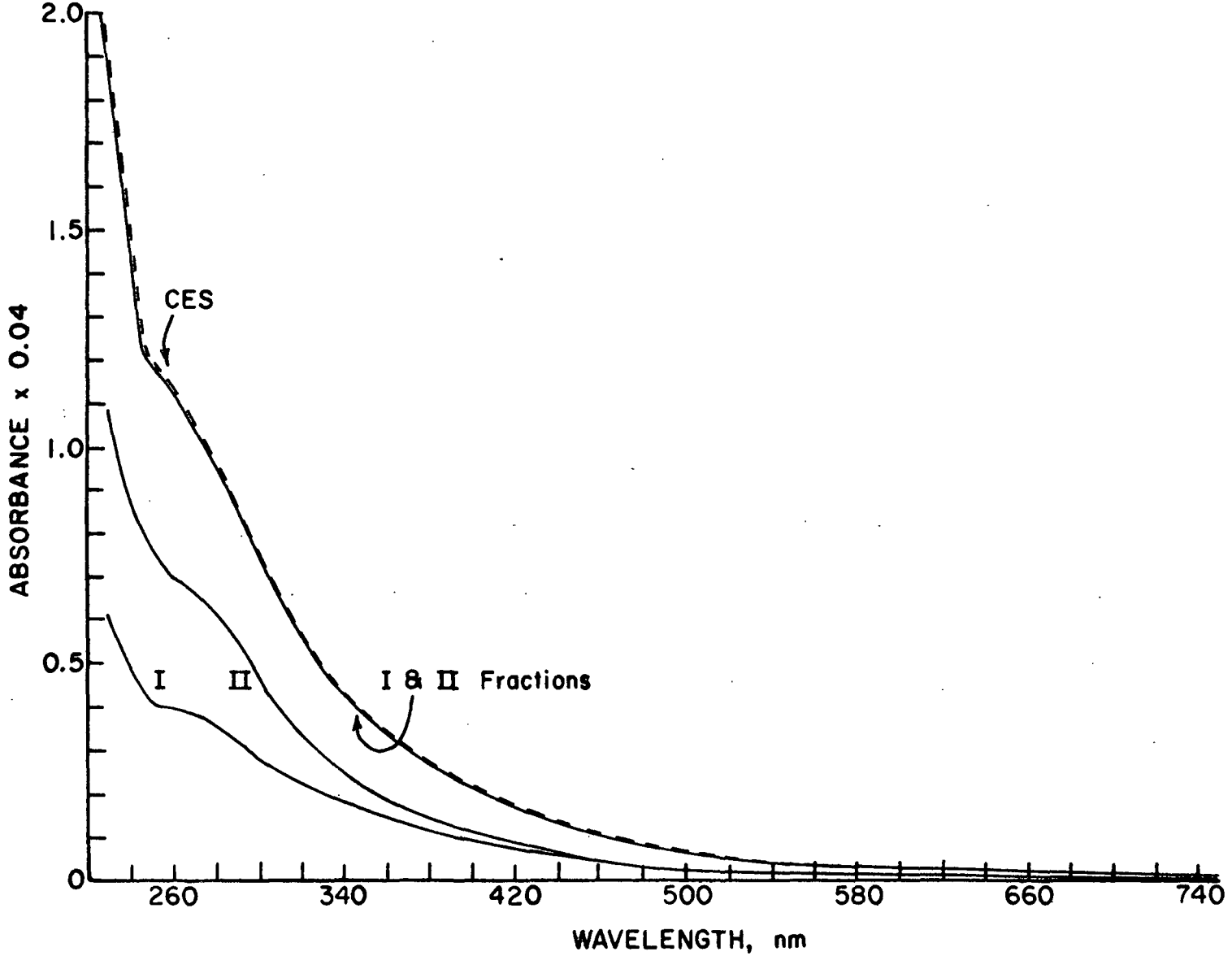

Figure 9. The Absorption Spectra of Fractions I, II, I & II, and CES at pH 7.5

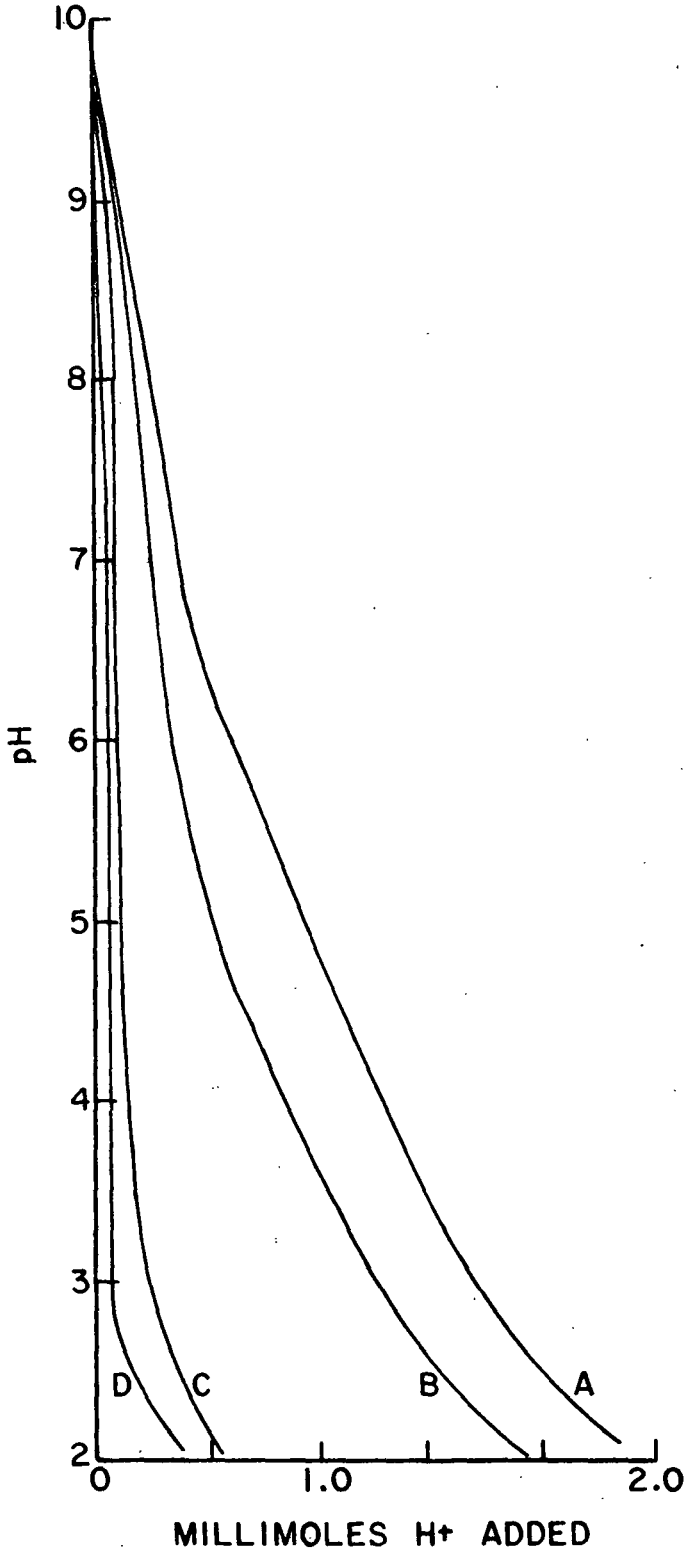

Figure 10. The Titration of CES and Fraction I with Hydrochloric Acid

(A: CES 0.91 g/50 ml; B: A after acidification and vacuum degassing with pH adjustment; C: Fraction I 0.091 g/50 ml; D: distilled water (50 ml) plus sodium hydroxide to pH 9.5)

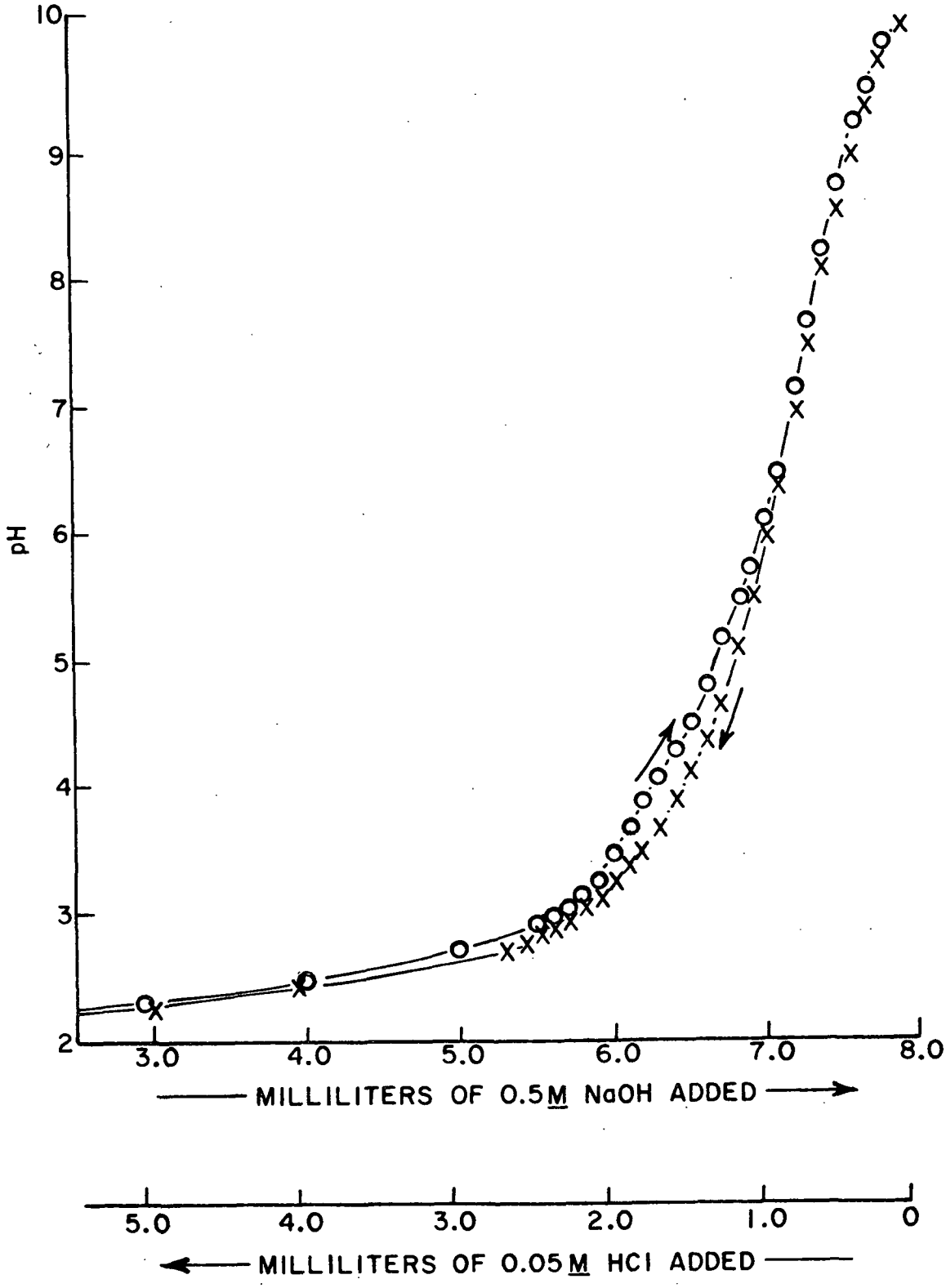

Figure 11. The Titration of Fraction I with Sodium Hydroxide and Hydrochloric Acid (0.454 g Fraction I/500 ml)

When the infrared spectra of both color body sources were compared at different pH's, it was apparent that CES also contained carboxylic groups with lower pK_a's than Fraction I. When Fraction I was at pH 3, the 1710 to 1720 cm^{-1} peak (Peak A), attributed to carboxylic functional groups, dwarfed the 1610 to 1630 cm^{-1} peak (Peak B) attributed to carboxylate (see Fig. 12). As the pH of Fraction I was raised the ratio of these peaks changed. At a pH between 4 and 5 they were of equal intensity and at pH 7 or above the 1610 to 1590 cm^{-1} peak (the carboxylate peak) completely dominated the spectrum in the regions mentioned. When CES was at pH 3, the carboxyl-carboxylate peaks were of about equal intensity, showing that CES had a greater proportion of ionized carboxylic groups than Fraction I. With increasing pH, the carboxylate peak completely dominated the carboxylic peak, far more than was observed for Fraction I.

The relative molecular weight distribution of Fraction I was investigated by gel permeation chromatography using Bio-Gel P-10*. This resin was chosen primarily because Crozier (30) used it to separate CES components (from the same effluent sample) during his investigation of the role of trace metals in caustic extract color. He found that the first material eluted (excluded) represented 60+% of CES color and had an apparent molecular weight, determined by sedimentation equilibrium, of about 10,000 (30). Figure 13 shows the elution profiles of CES, Fraction I, and Fraction II. The elution profiles indicate that Fraction I was enriched with higher molecular weight species; however, it was evident that the acid precipitation was not extremely selective because Fraction II also contained some of the higher

*Porous beads of polyacrylamide, molecules over ca. 10,000 molecular weight are excluded.

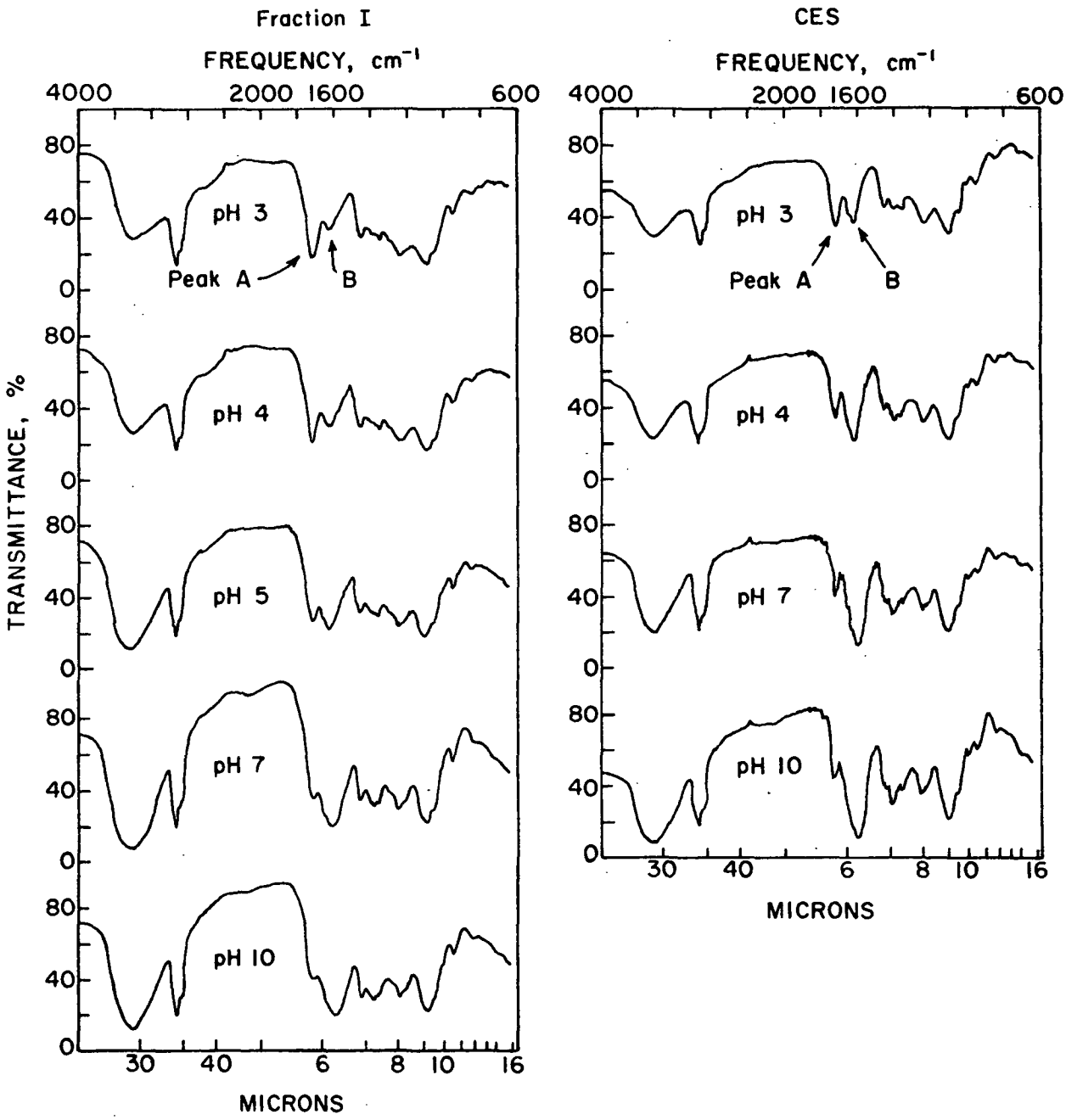

Figure 12. The Infrared Spectra of Fraction I and CES at Various pH's

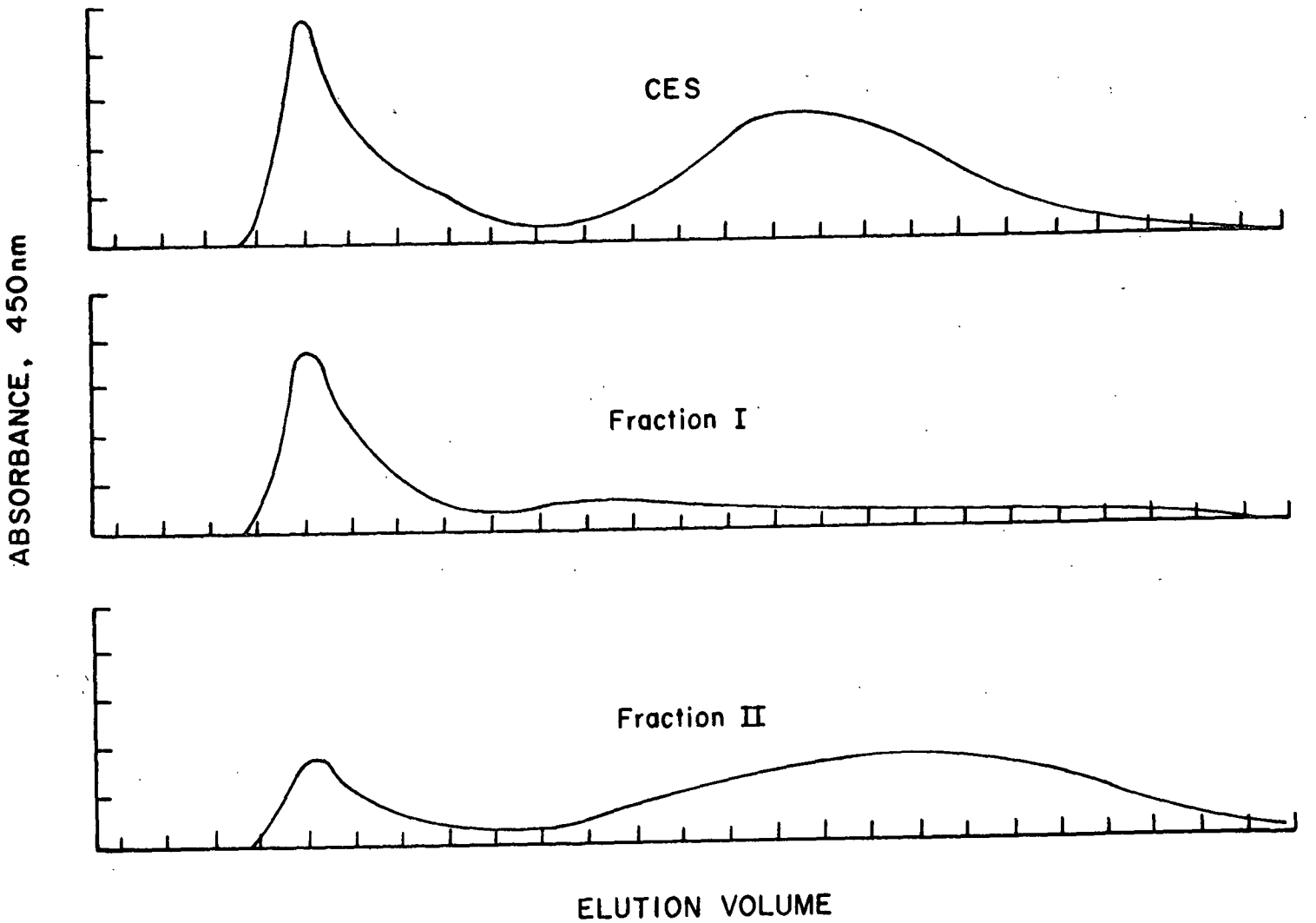

Figure 13. The Elution Profiles of Fractions I, II and CES Through Bio-Gel P-10

molecular weight CES components. Presumably the reason that the high molecular weight Fraction II material did not precipitate is because it contained more ionized anionic groups than Fraction I.

Recombined Fractions I and II were tested for color removal using diethylenetriamine at pH 4, tetraethylenepentaamine at pH's 4, 5, 6, and 8, and PEI 18 at pH 7.5 (Fig. 14). In each case the color removal profiles observed were within 7% of the maximum color removal observed with CES.

From these data and the observations of Dugal, et al.*, it was concluded that the acid precipitation did not appreciably alter the general character of CES components. It is quite possible, however, that some minor changes resulting from acid-catalyzed hydrolysis may have occurred.

COLOR REMOVAL FROM FRACTION I

COLOR REMOVAL FROM FRACTION I BY BRANCHED POLYAMINES

Color removal from Fraction I by PEI 18 at various pH's and polyamine concentrations is shown in Fig. 15 and 16. As observed with CES, the precipitation of color bodies was dependent upon both the pH of the precipitating medium and the polyamine concentration. However, Fraction I color bodies appeared to be far more easily precipitated than those of CES, and almost 100% color removal could be obtained throughout the pH range tested (pH 4 through 9). The effect of decreasing pH was to decrease the polyamine concentration required to achieve maximum color removal; for instance, 4 meq N/liter at pH 9 versus 1 meq N/liter at pH 4. As before, the presence

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* Dugal, et al. have shown that acid precipitation of caustic extract color bodies had little effect on color body absorptivity or sedimentation coefficient (11).

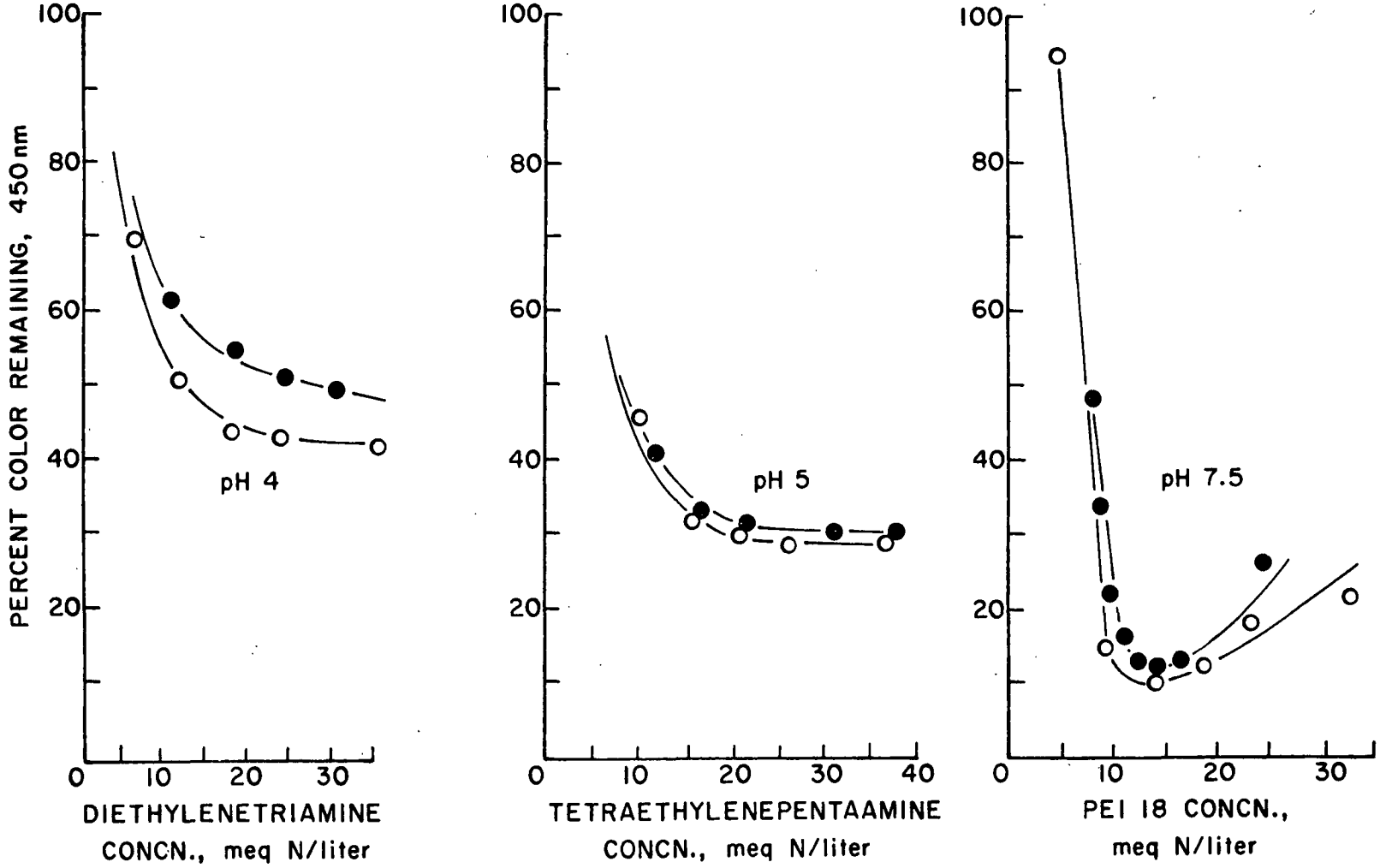


Figure 14. Color Removal from Recombined Fractions I and II and from CES by Various Polyamines at Their pH Optima

(o, Recombined Fractions I and II; •, CES)

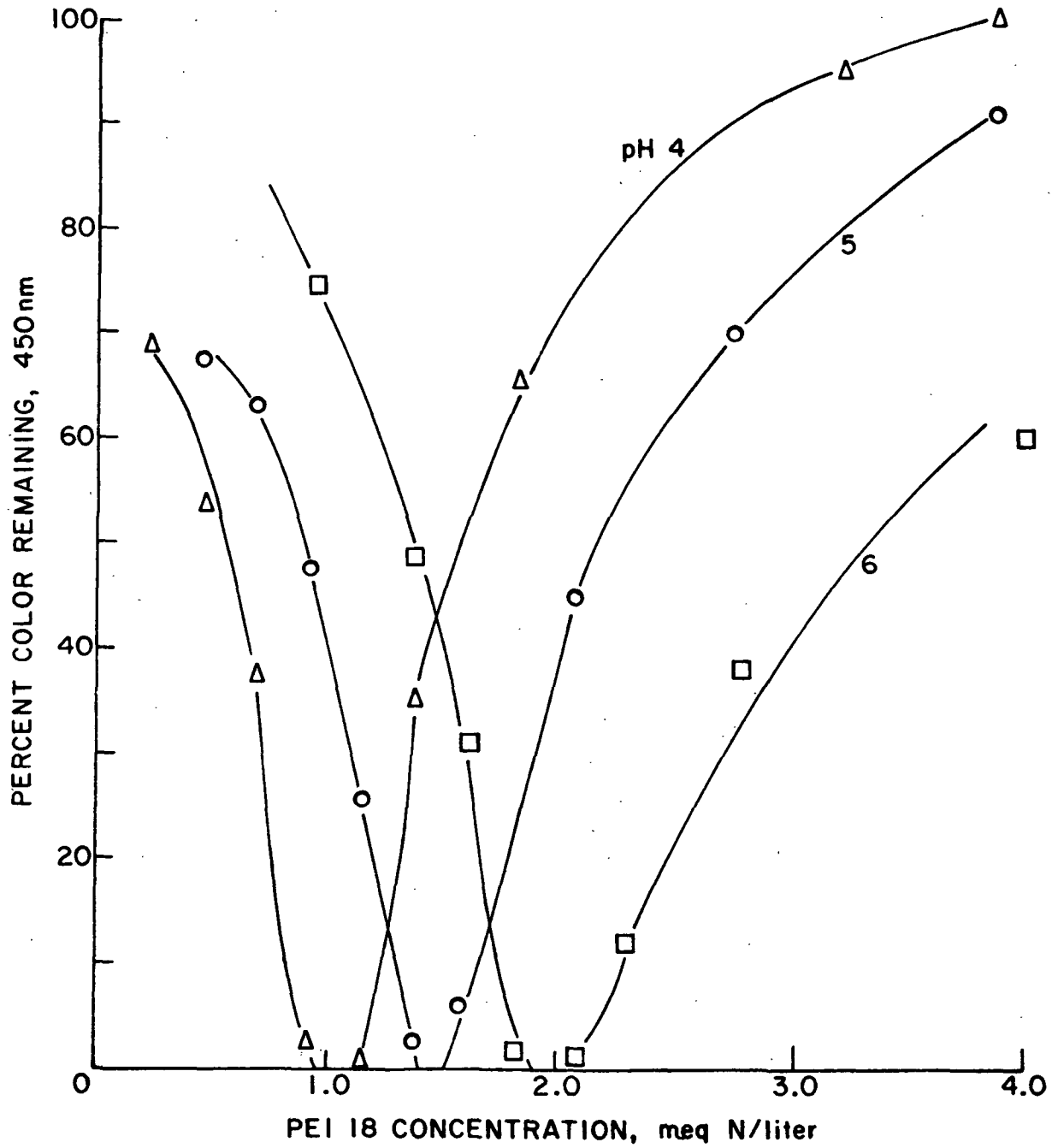


Figure 15. Color Removal from Fraction I by PEI 18, pH 4, 5 and 6

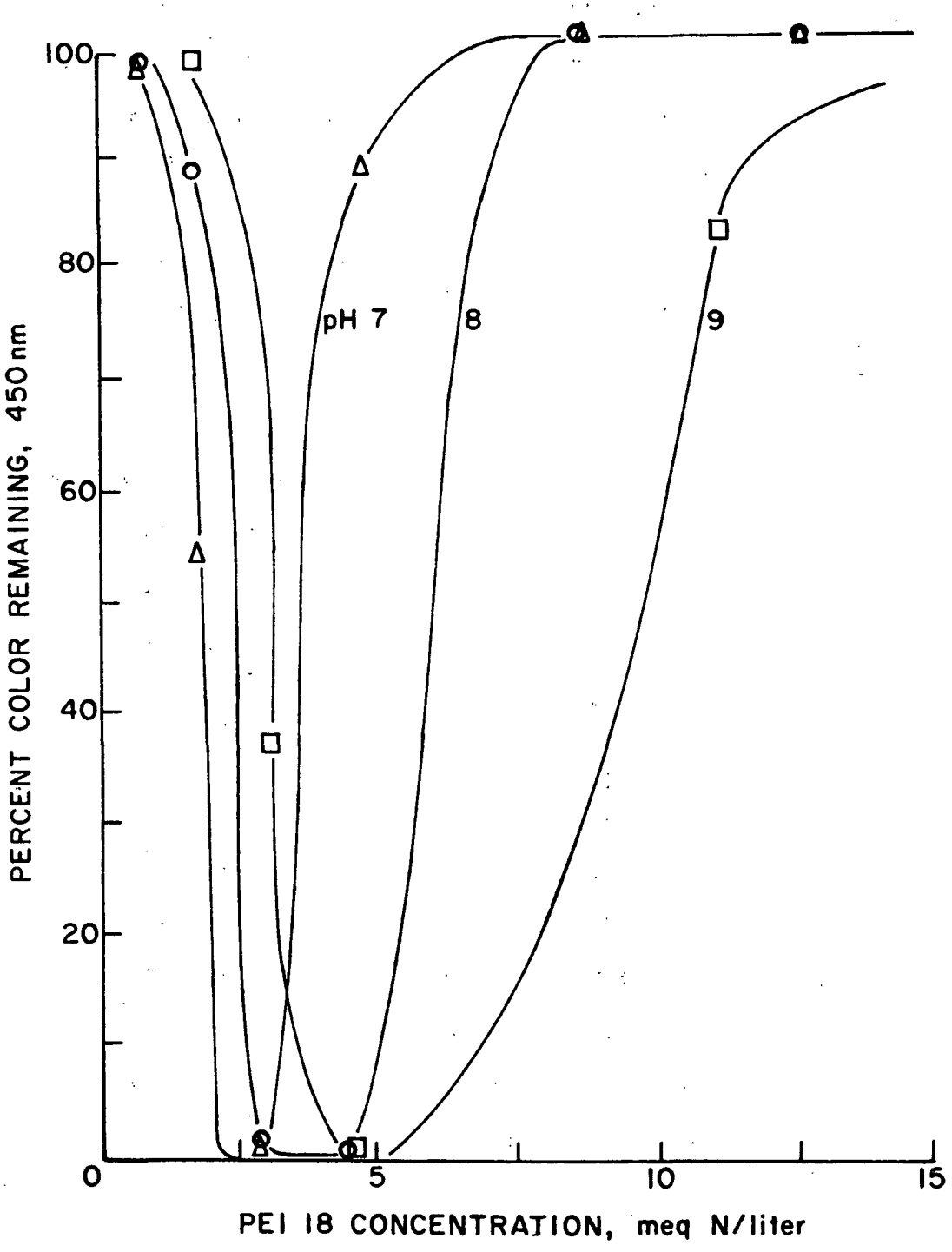


Figure 16. Color Removal from Fraction I by PEI 18 at Neutral and Alkaline pH's

of excess polyamine decreased the amount of color removal observed but, with Fraction I, the effect was far more apparent, since color removal curves went from 100% color remaining to zero and then back to 100%. It was also apparent that the decrease in color removal observed was far more rapid at acidic pH's than at alkaline pH's.

Color removal from Fraction I by PEI 12 is shown in Fig. 17. At pH's 7 and 8, the color removal curves obtained were similar to those observed with PEI 18. This was not the case at pH 9, where excess polyamine decreased color removal, but only slightly in comparison to that observed with PEI 18. Color removal by PEI 6 is also shown in Fig. 17. In this case color removal was relatively insensitive to the presence of excess polyamine at the pH's tested, 7 through 9. From these data it appears likely that the change in the shape of the Fraction I color removal curves is caused by changes in the number of protonated amino groups per molecule.

COLOR REMOVAL FROM FRACTION I BY LINEAR POLYAMINES

The color removal curves for tetraethylenepentaamine are shown in Fig. 18. Once again, Fraction I color bodies proved to be far more easily precipitated than those of CES. The effect of decreasing pH was to decrease the polyamine concentration required to achieve maximum color removal. As in the case of the branched polyamines, the maximum color removal levels observed were approximately the same at all pH's, although there was a slight trend toward lower color removal as the precipitation medium became less acidic.

Figure 18 also shows color removal from Fraction I by diethylenetriamine. The curves observed were different from those for tetraethylenepentaamine or the branched polyamines in that ultimate color removal was very much

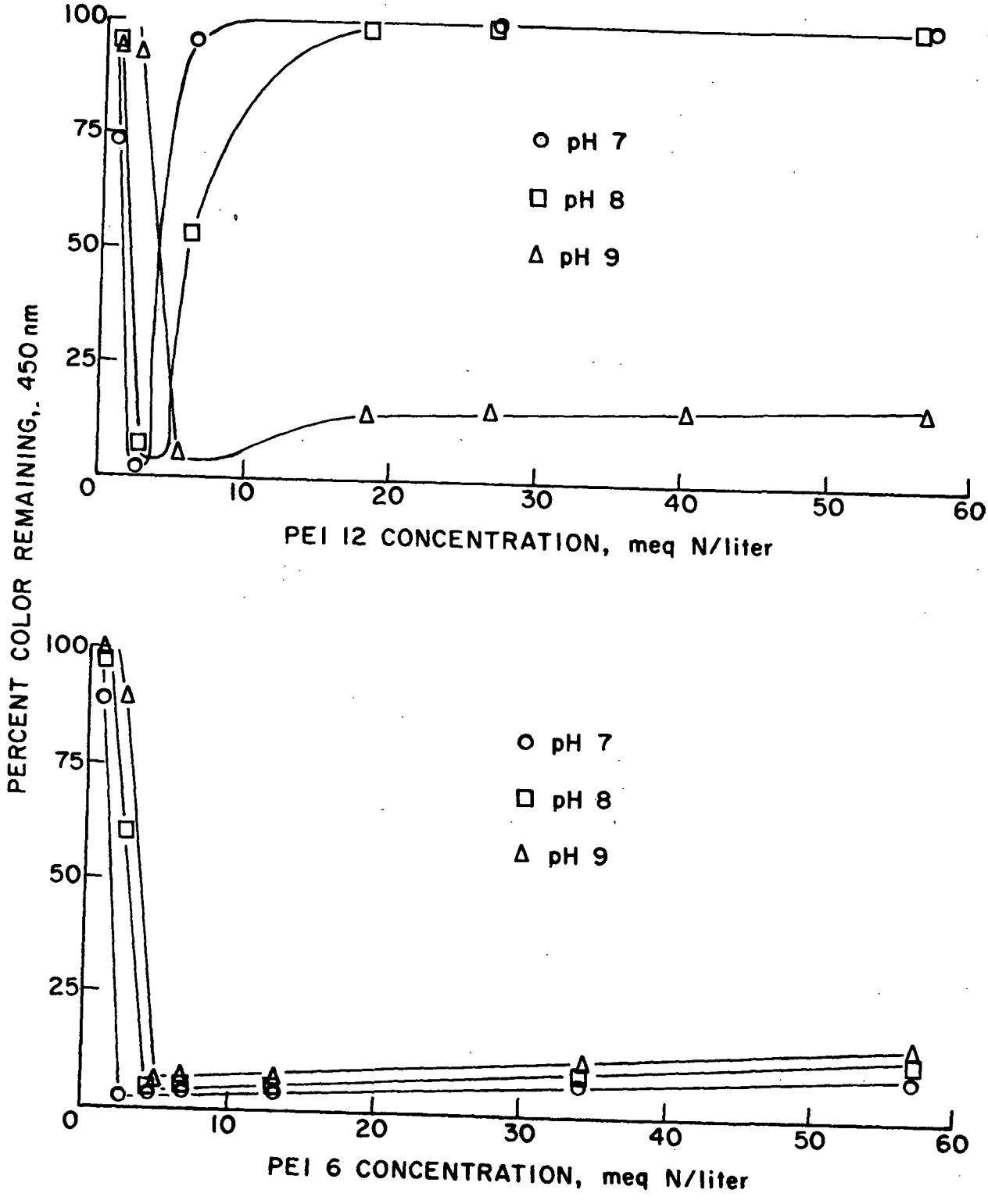
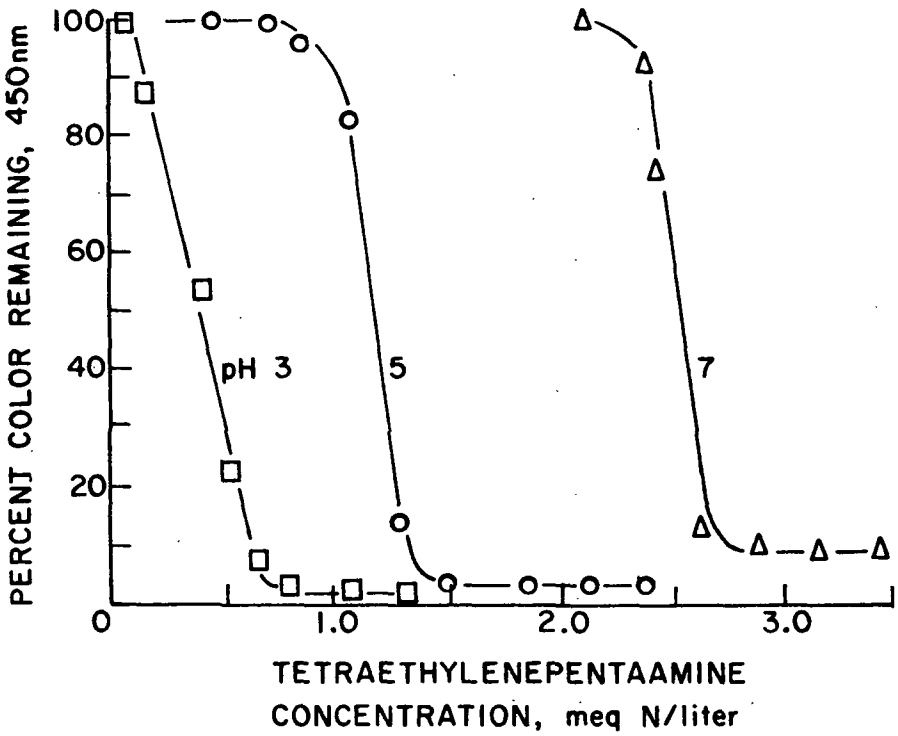


Figure 17. Color Removal from Fraction I by PEI 12 and 6



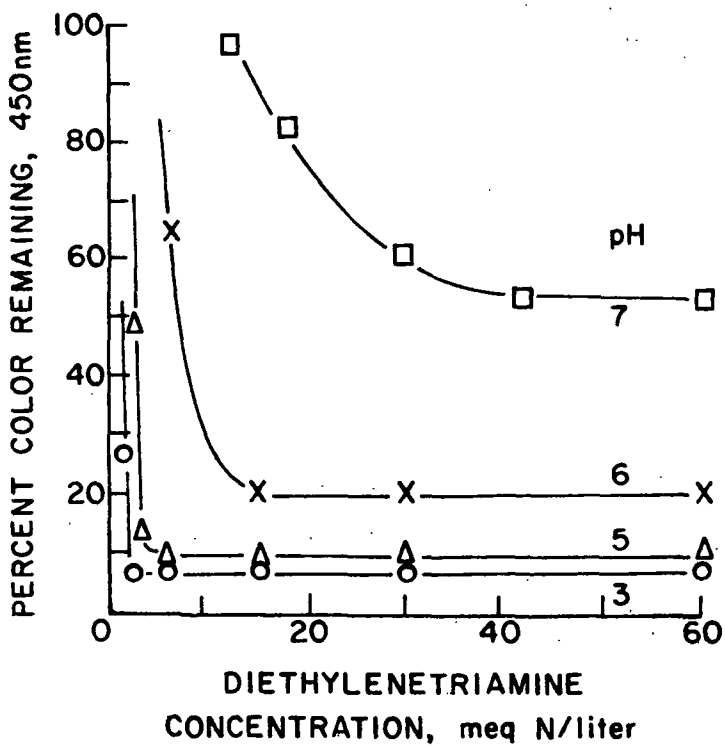


Figure 18. Color Removal from Fraction I by Linear Polyamines

dependent upon pH. When the pH was 7, only about 50% color removal was observed. As the pH of the precipitation medium was decreased, color removal increased, and at pH's below 5, about 90% color removal was attained, and the concentration required to achieve maximum color removal decreased 15-fold from ca. 45 meq N/liter at pH 7 to 3 meq N/liter at pH 3. Since Fraction I characteristics should be constant at a given pH, the differences in color removal curves for tetraethylenepentaamine and diethylenetriamine are probably attributable to differences in the polyamines. The most significant differences between the two amines are chain length and the number of amino and protonated amino groups per molecule.

COLOR REMOVAL FROM FRACTION I BY DIAMINES

The enhanced polyamine precipitability of Fraction I color bodies compared to CES has already been mentioned. However the phenomenon was even more evident with the diamines. Figure 19 shows color removal from Fraction I by ethylenediamine and its symmetrical N-methylated analogs, N,N'-dimethyl-, N,N,N',N'-tetramethyl-, and hexamethylethylenediammonium diiodide. The substituted diamines, previously ineffective with CES, removed significant amounts of Fraction I color. At pH 4, all the analogs were able to precipitate color but their effectiveness decreased with increasing methyl substitution. As the pH of the precipitation medium increased, color removal decreased and, at pH 6, only ethylenediamine and N,N'-dimethylethylenediamine removed color. At pH 8, none of these diamines were effective.

This series of experiments showed that color body ionic character is also important in precipitation. This can be inferred from the fact that color removal by the bisquaternary ammonium salt decreased with increasing pH.

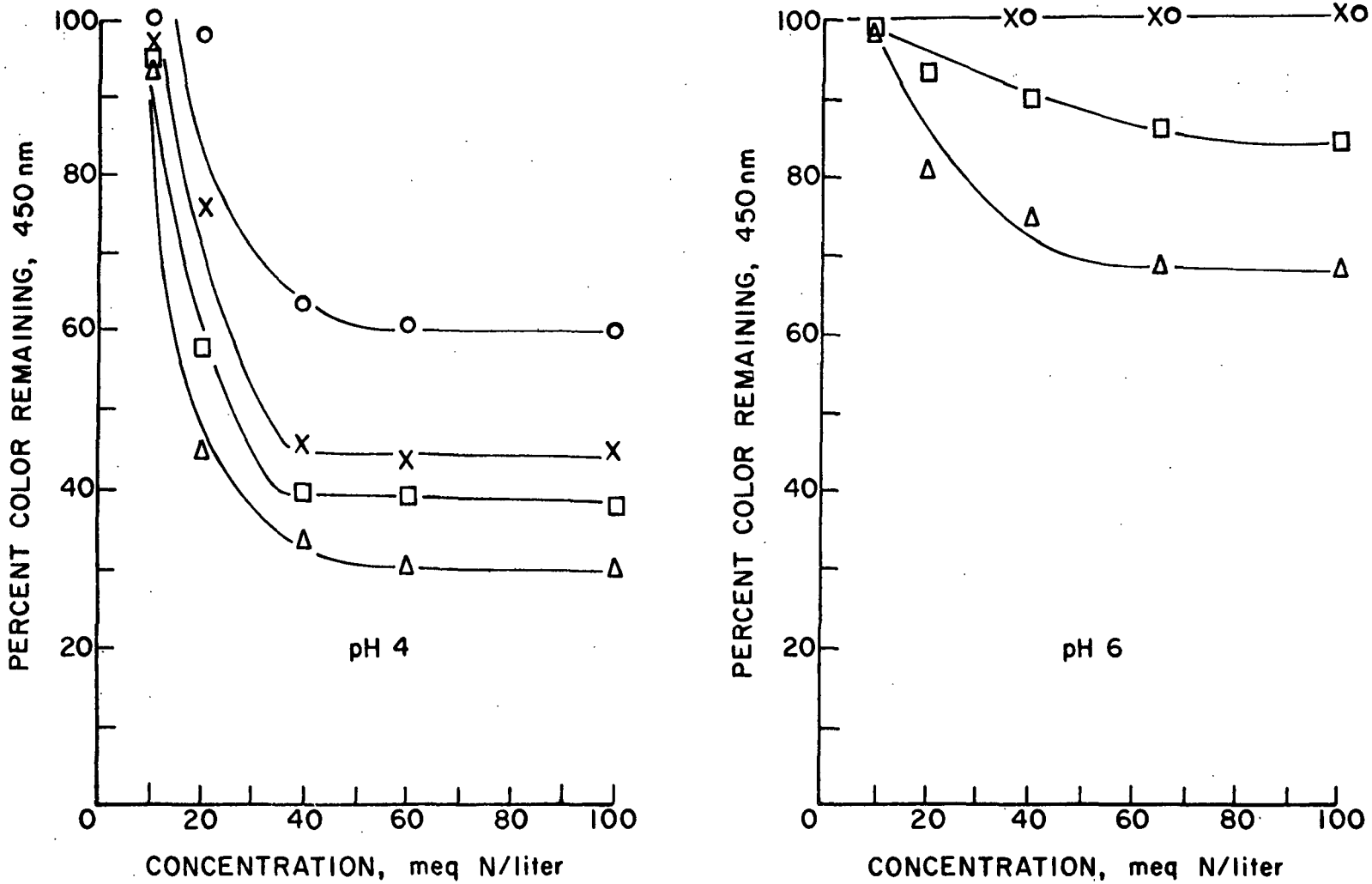


Figure 19. Color Removal from Fraction I by Ethylenediamine and its Symmetrical, N-Methyl Substituted Analogs

(Δ Ethylenediamine, □ N,N'-Dimethylethylenediamine, x N,N,N',N'-Tetramethylethylenediamine, o Hexamethylethylenediammonium diiodide)

Since the ionic character of the quaternary salt is independent of pH, the differences in color removal must be attributed to ionic changes in the other precipitate constituent: the color bodies.

In order to examine the effects of charge separation on color removal from Fraction I by the diamines, 1,3-diaminopropane and 1,4-diaminobutane were tested and the results obtained are shown in Fig. 20, along with ethylenediamine. These diamines removed significant amounts of Fraction I color even though they were completely ineffective against CES color (p. 21). The effect of increasing the carbon chain length from two to three to four carbons was to decrease maximum color removal from 70 to 50% and to increase the solution concentration required to achieve maximum color removal. However, as in the case of CES (p. 21), 1,12-diaminododecane reversed this trend, being quite effective over a wide pH range (Fig. 21). The effect of increasing pH was to slightly increase the concentration of 1,12-diaminododecane required to achieve maximum color removal. Since the percent protonation of this amine is essentially 100% over the pH range tested (pH 4 to 8), the differences observed may be attributed to changes in the color body character.

PRECIPITATE POLYAMINE CONTENT

In the experimental program initially proposed, the polyamine content of color body precipitates was to be determined by total nitrogen analysis of the precipitates. This approach assumed that the CES nitrogen content would be negligible, an assumption proven to be incorrect when CES was found to have a nitrogen content of 88 ppm (Table II) or 0.97% of the freeze-dried solids. Finding an appreciable nitrogen content in caustic extract effluent is not without precedent, as Dugal (11) reported the presence of

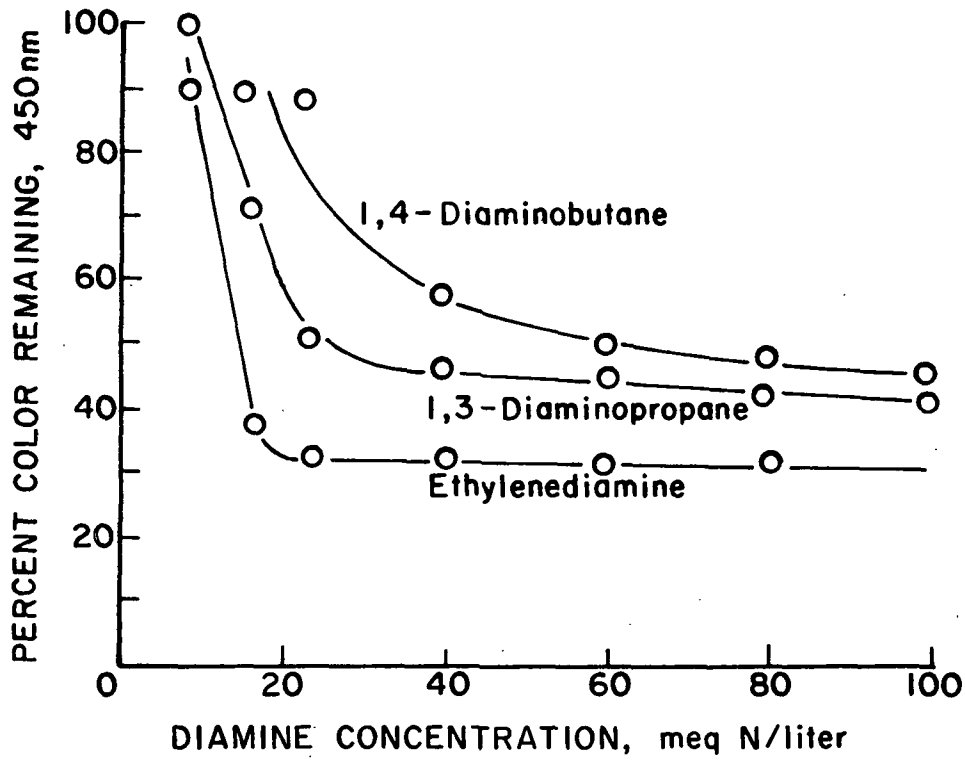


Figure 20. Color Removal from Fraction I by Short Chain Diamines at pH 4

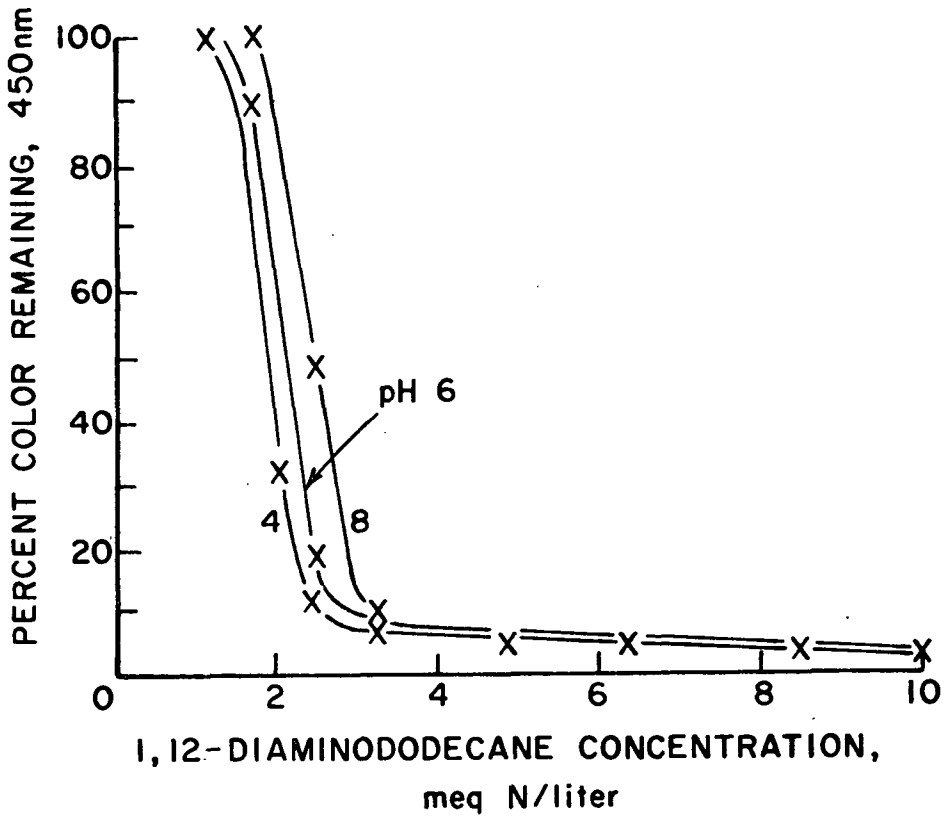


Figure 21. Color Removal from Fraction I by 1,12-Diaminododecane

nitrogen in the caustic extract effluent sample he investigated. He identified the nitrogen as ammonium chloride and speculated that its presence might be an artifact from the column chromatography through the polyacrylamide resin he employed. Clearly, this explanation would not be applicable in the present case. However wood does contain nitrogen (47), and it is possible that this nitrogen may actually be released during the bleaching process.

Since total nitrogen analysis could not distinguish polyamine nitrogen from CES nitrogen, there was a possible error of up to 6 meq N/liter if the total nitrogen analysis was the only analytical procedure employed; CES nitrogen was assumed to be quantitatively precipitated. While this assumption was unlikely to be correct in light of Dugal, et al.'s findings it was, nevertheless, desirable to determine polyamine content by some other method which was specific for polyamines.

Lindquist (29) determined PEI concentrations by spectrophotometry, measuring the increase in ultraviolet absorbance due to the formation of cupric ion-polyamine complexes. His method was modified and used to determine polyamine concentration in supernatants from color removal experiments (see Appendix IV for the development of the assay).

Table VI shows the results obtained when both methods were used to determine the polyamine content of the same samples of several CES and Fraction I precipitates. Although there was a tendency for the polyamine content determined by spectrophotometry to be slightly higher than that obtained by total nitrogen analysis, the values obtained by both methods were in general agreement, indicating that CES nitrogen did not constitute an appreciable portion of the precipitate.

TABLE VI

THE POLYAMINE CONTENT OF SEVERAL FRACTION I AND CES PRECIPITATES[a]

Color Source	Precipitation Conditions	Percent Color Removal[b]	Precipitate Dry Weight, mg[c]	Precipitate Polyamine Content[c] Determined: Nitrogen Analysis, meq N	Precipitate Polyamine Content[c] Determined: Spectrophotometry, meq N
Fraction I	PEI 18 2.75 meq N/liter, pH 7	99 (40)	760 (1900)	2.6 (6.5)	2.8 (7.0)
CES	PEI 18 13.6 meq N/liter, pH 7	89	2200 (2480)	13.0 (14.6)	12.6 (14.2)
Fraction I	Tetraethylenepentaamine 3.98 meq N/liter, pH 5	97 (39)	660 (1700)	1.2 (3.1)	1.3 (3.3)
CES	Tetraethylenepentaamine 15.8 meq N/liter, pH 5	70	1270 (1810)	2.4 (3.4)	2.6 (3.7)
Fraction I	Diethylenetriamine 3.00 meq N/liter, pH 4	92 (37)	630 (1710)	0.65 (1.8)	0.69 (1.9)
CES	Diethylenetriamine 36.0 meq N/liter, pH 4	52	903 (1740)	1.03 (1.98)	Not determined

[a] Normalized to an initial precipitation volume of one liter.

[b] Values shown in the parentheses are the percent of CES color removed.

[c] Values shown in the parentheses are normalized to 100% color removal from CES (p. 52).

Having established that either analytical technique could adequately estimate precipitate polyamine content, it was now possible to compare Fraction I and CES precipitate compositions provided the data were expressed on a common basis. The basis chosen was 100% color removal from 1 liter of CES. This could be done by expressing Fraction I color removal in terms of CES color removal, for example: 100% color removal from Fraction I would be equivalent to 40% (p. 31) color removal from CES. Then precipitate dry weight and polyamine content were multiplied by the quotient obtained by dividing percent CES color removal into 100%. When the data are normalized in this manner the calculated values for CES and Fraction I would be identical if color removal from Fraction I was directly proportional to color removal from CES and there was no experimental error. The values calculated in this manner are shown in parentheses in Table VI.

When the data for diethylenetriamine were treated in this manner Fraction I precipitate dry weight was equivalent to 1710 mg, which was quite similar to the 1740 mg value calculated for the CES precipitate. The Fraction I precipitate polyamine contents determined by total nitrogen analysis and spectrophotometry became 1.76 and 1.87 meq N, respectively, which was within 11% of the 1.98 meq N calculated from the CES precipitate polyamine content determined by nitrogen analysis.

When the data for tetraethylenepentaamine were expressed in this manner, Fraction I and CES precipitate dry weights became 1710 and 1810 mg, respectively. The Fraction I and CES precipitate polyamine content determined by nitrogen analysis became 3.09 and 3.35 meq N and the values determined by spectrophotometry became 3.34 and 3.78 meq N. These data showed that Fraction I and CES precipitate dry weight and polyamine content were roughly proportional to percent color removal by the linear polyamines, and this observation suggested

that the color body species being precipitated from Fraction I and CES had the same general properties.

When the Fraction I-PEI 18 precipitate weight was calculated, the resulting 1900 mg value was about 20% less than the 2200 mg value calculated for the CES-PEI 18 precipitate. However, when the precipitate polyamine contents were compared (Table VI), the 6.5 and 7.0 meq N for Fraction I were less than half the CES precipitate polyamine contents of 14.6 and 14.2 meq N. Color removal from CES by PEI 18 was not proportional to color removal from Fraction I by PEI 18. These data suggested that there were certain precipitable CES species which required far more PEI than the average Fraction I precipitable species, and that these alleged components which required the extra PEI 18 were not precipitated by the linear polyamines.

THE NATURE OF CES PRECIPITABLE COMPONENTS

The possible existence of two general types of precipitable CES species was alluded to earlier during the discussion of the changes in color removal/precipitate dry ratios (p. 23). Reiterating, the observations were that as excess PEI 18 was added to CES, color removal decreased more rapidly than precipitate weight. At that time polyamine contents were not given and further discussion was deferred. At this point let us resume that discussion.

Table VII shows the effects of increasing PEI 18 concentration on color removal from CES and includes precipitate polyamine content. As the initial PEI 18 concentration was increased from 13.6 to 57 meq N/liter, precipitate dry weight decreased 16%, from 2170 to 1810 mg, precipitate polyamine content decreased 7%, from 12.6 to 11.7 meq N, but percent color removal decreased from 84.7 to 46.5%. Since color removal decreased more than

precipitate dry weight and polyamine content, precipitate composition must have changed. Apparently the color bodies that precipitated at optimum PEI 18 concentrations were being replaced by less chromophoric CES components which required more PEI 18. An alternative interpretation which would attribute the apparent loss of color removal to the formation of chromophoric, nonprecipitating PEI-CES complexes was considered unlikely since precipitate weights decreased to zero when larger excesses of PEI 18 were added and total absorbance at 450 nm returned to the original levels.

TABLE VII

THE EFFECTS OF INCREASING POLYAMINE CONCENTRATION ON THE POLYAMINE CONTENT OF CES PRECIPITATES

Precipitant	Polyamine Concentration		Color Removal, %	Precipitate	
	ppm	meq N/liter		Dry Weight, mg[a]	Polyamine Content, meq N[a]
PEI 18 (pH 7)	400	9.1	40.6	1400	6.4
	600	13.6	84.7	2170	12.6
	800	18.2	77.6	2300	12.7
	1600	36.4	50.1	2000	12.4
	2500	57.0	46.5	1810	11.7
Tetraethylene-pentaamine (pH 5)	400	10.6	69.5	1280	2.5
	600	15.8	70.5	1270	2.6
	1200	31.6	70.0	1310	2.7
	2500	66.1	68.8	1290	2.6

[a]Normalized to a reaction volume of 1 liter.

Table VII also shows the effects of increasing tetraethylenepentaamine concentration from 10.6 to 66 meq N/liter on CES color removal, precipitate dry weight, and precipitate polyamine content. In this case the three parameters remained fairly constant, suggesting that precipitate composition was not

appreciably affected by the presence of excess tetraethylenepentaamine. However, visual observation indicated that the rate of precipitation increased with increasing polyamine concentration.

Thus it appeared as though color removal from CES involved the precipitation of two types of precipitable materials, those with average color and solubility properties much like Fraction I, which could be precipitated by both the linear and branched polyamines, and those species which were soluble at pH 1 and were precipitated only by the larger, branched polyamines. At this point it was decided that further attempts to probe the role of charge and mechanism of precipitation would be confined to the precipitation of Fraction I type color bodies, because they appeared to represent 70% of the original CES color (p. 53) and contained less nonprecipitable material (p. 31).

THE POLYAMINE CONTENT AS A FUNCTION OF pH

The next step in the investigation was to further relate precipitate polyamine content to color removal. Color removal from Fraction I at pH 4 was arbitrarily chosen as a starting point, and Table VIII shows the polyamine content of various precipitates expressed as millimoles of polyamine, milliequivalents of nitrogen, and milliequivalents of ammonium ion, assuming constant ionic character for the amine in the presence of the color bodies. So that comparisons can be made, the data have been normalized to 100% color removal from 1 liter of Fraction I.

When the precipitate polyamine contents were expressed as millimoles, the values varied over 15-fold, from 0.026 mM for PEI 18 to 0.32 mM for ethylenediamine. When these same precipitate polyamine contents were expressed as milliequivalents of nitrogen, the range decreased to a factor of

about 1.7, with 1.09 meq N for PEI 18 versus 0.64 meq N for ethylenediamine. However, when the data were expressed as milliequivalents of ammonium ion, the values for each precipitate were approximately the same, about 0.63 meq of ammonium ion. The amount of amine in the precipitate appeared to be directly related to the initial cationic character of the amine.

TABLE VIII

THE POLYAMINE CONTENT OF VARIOUS FRACTION I pH 4 PRECIPITATES[a]

Polyamine	Millimoles	Nitrogen, meqs	Ammonium ion[b], meqs
Ethylenediamine	0.32	0.64	0.64
1,12-Diaminododecane	0.33	0.66	0.66
Diethylenetriamine	0.24	0.72	0.62
Tetraethylenepentaamine	0.17	0.85	0.61
PEI 18	0.026	1.09	0.67

[a]Normalized to 100% color removal from 1 liter of Fraction I.
[b]Assuming the cationic character of the polyamine in solution.

Table IX shows the ammonium ion content of Fraction I precipitates obtained at other pH's. Again, the data have been normalized to 100% color removal from 1 liter of Fraction I.

As before, the ammonion ion content of Fraction I precipitates obtained at a given pH is approximately the same for each of the amines tested. However, the values increased about 50% when the pH of the precipitation medium was increased from 4 to 7. For PEI 18, the increase was from 0.67 meq of ammonium ion at pH 4 to 1.11 meqs at pH 7. When diethylenetriamine was the precipitant, the increase was from 0.62 meq of ammonium ion at pH 4 to 0.96 meq at pH 7. Since increasing pH decreases polyamine protonation, the observed

increase in precipitate ammonium ion content with increasing pH implied that precipitate polyamine cation content was determined by some other factor(s) which varied with pH. The likely candidate for this proposed determinant was the color body fraction because (1) it was a coreactant and (2) as was shown in Fig. 11, its anionic character increased with increasing pH. The increase in protanatable groups in Fraction I as a function of pH is also shown in Table IX.

TABLE IX

THE POLYAMINE CONTENT OF VARIOUS FRACTION I PRECIPITATES[a]

	Milliequivalents of Protonatable Groups[b] in Fraction I	Milliequivalents of Ammonium Groups[c] in Precipitates			
		PEI 18	Tetraethylene-pentaamine	Diethylene-triamine	1,12-Diamino-dodecane
pH 7	1.31	1.11	0.99	0.96	0.92
pH 6	1.08	0.90	0.88	--	--
pH 5	0.89	0.73	0.77	0.63	--
pH 4	0.58	0.67	0.61	0.62	0.66

[a] Normalized to 100% color removal from 1 liter of Fraction I.

[b] Assuming complete protonation at pH 2.

[c] Assuming the cationic character of the polyamine in solution.

As can be seen, the cation/anion ratio approaches one, strongly suggesting that charge neutralization may be an important part of the mechanism of precipitation. However, before trying to infer anything about the exact precipitate stoichiometry, it should be pointed out that the Fraction I anionic character shown in Table IX assumed complete protonation at pH 2. Based upon what is known of caustic extract effluent acidity (9), this assumption is not completely correct, and consequently, Fraction I color bodies are probably more anionic than indicated in Table IX. Another point which should be raised is the fact

that the precipitation of Fraction I components was not quantitative, and certainly a small portion of the acidity remained in solution. This would tend to shift the apparent balance toward the cationic polyamine. The exact extent to which these factors affected the precipitate stoichiometry was unknown. However, even if the ionic character of the color bodies undergoing precipitation could be accurately determined, there was no reason to assume that the same ionic stoichiometry would be found in the precipitate because of the possibility of proton transfer from a cationic group to an anionic group to yield two uncharged moieties. Thus the next phase of the problem was to investigate the final ionic character of the precipitate.

INFRARED SPECTROSCOPY OF COLOR BODY-POLYAMINE PRECIPITATES

The problem of establishing the ionic character of the precipitate was approached using infrared spectroscopy. The line of reasoning was as follows. In earlier work (Fig. 12) it was shown that the IR spectrum of Fraction I was strongly dependent upon pH, the dependency being such that each pH had a characteristic carboxyl/carboxylate ratio. Therefore, by observing the ratio of these peaks in the precipitate, one could estimate the relative carboxyl/carboxylate ratio.

It was thought that it would be possible to detect any large changes in the carboxyl/carboxylate ratio which might result from extensive proton transfer. This approach had some inherent problems in that it included an assumption that the contribution to the infrared peaks of interest from the polyamine could be neglected. Preliminary data showed that this might not be valid, as the amine absorbed throughout the range of interest (Fig. 22a). But, in some cases the amine was only a minor component of the precipitate; for instance, the pH 4 diethylenetriamine precipitate was only 3.5% polyamine,

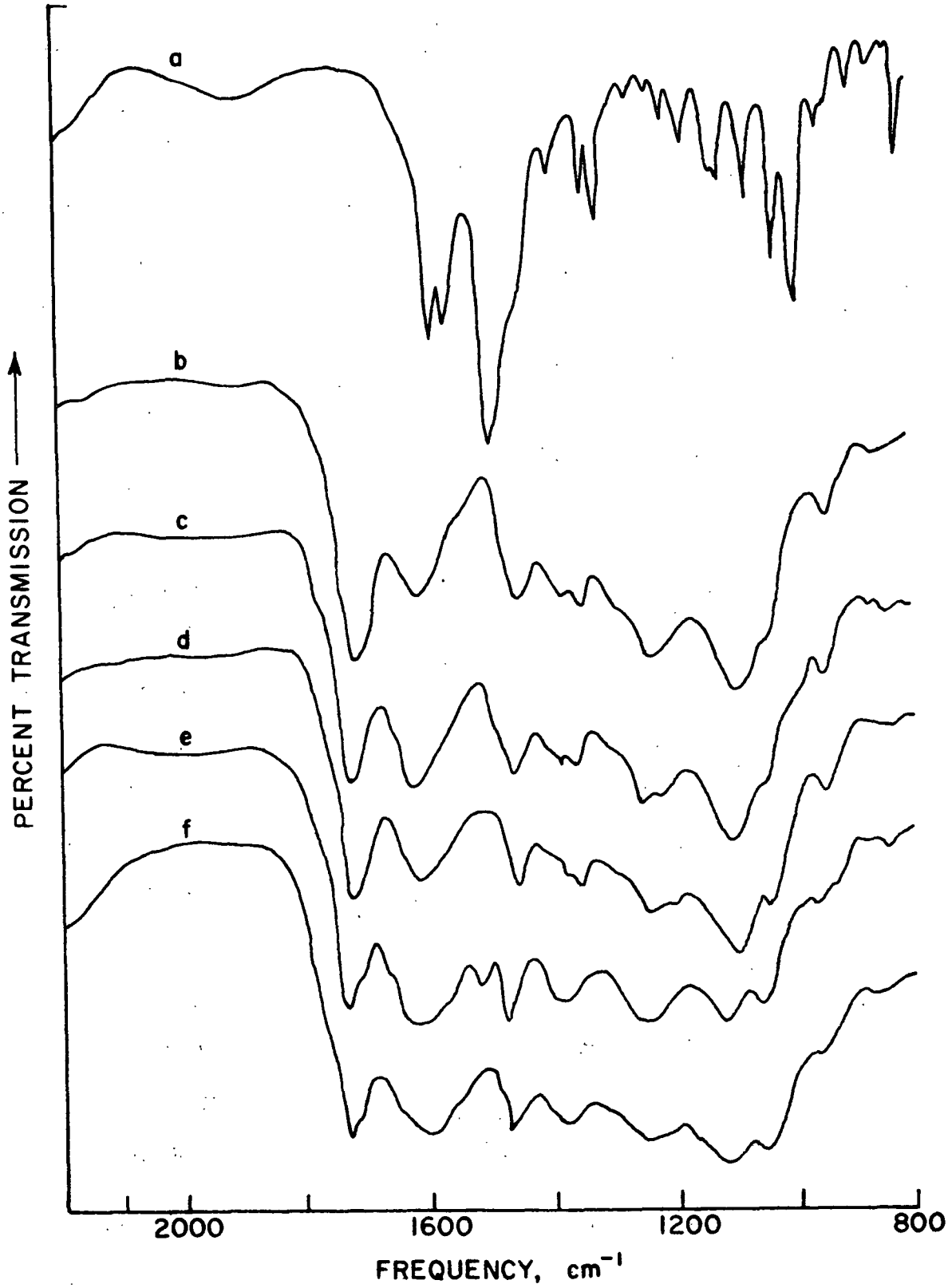


Figure 22. The Infrared Spectra of Several pH 4 Color Body Precipitates

(a: Diethylenetriamine pH 4; b: Fraction I; c: 92% Fraction I, 8% Diethylenetriamine pH 4; d: Diethylenetriamine-Fraction I color body precipitate; e: Diethylenetriamine-CES color body precipitate; f: PEI 18-Fraction I color body precipitate)

and therefore the presence of the polyamine might not have a significant effect on the infrared spectrum. To explore this possibility the infrared spectrum of a freeze-dried sample of Fraction I at pH 4 was determined (Fig. 22b) and then that KBr pellet was broken up and reground; then a sample of diethylenetriamine, which had been obtained by freeze-drying a pH 4 solution of the polyamine, was added, and the resulting mixture was pressed into a pellet. The amount of diethylenetriamine added was such that the final composition of the sample was that found in the pH 4, diethylenetriamine-Fraction I precipitate. The infrared spectrum of this mixture is shown in Fig. 22c..

Comparison of Fig. 22b and c shows that the addition of the polyamine did increase the absorbance of the Fraction I sample. The increase was most evident in the 1400 to 1600 cm^{-1} region, and the net result was to decrease the apparent carboxyl/carboxylate ratio such that it appeared to be that of a Fraction I sample at a pH between 4 and 5. Figure 22d shows the spectrum of a pH 4 diethylenetriamine-Fraction I color body precipitate. As might have been expected, the spectrum is very similar to but not identical to that of 22c. The Fraction I carboxylate peak was slightly lower than the corresponding peak in the mixture. This can, in all likelihood, be attributed to the lack of quantitative precipitation. From these observations, it seemed reasonable to conclude that the precipitated color body-polyamine complex retained the most of the initial ionic character of the components. The other polyamine color body precipitates showed similar spectral changes.

Figure 22e shows the spectrum of a pH 4 diethylenetriamine-CES precipitate. As can be seen, the spectrum is quite similar to the corresponding Fraction I precipitate (22d) despite the considerable differences between Fraction I and CES. This observation is in complete agreement with the previous conclusion that the composition of pH 4, CES and Fraction I diethylenetriamine precipitates were quite similar.

Figure 22f shows the spectrum of a PEI 18-Fraction I pH 4 precipitate. This spectrum is quite similar to those already mentioned, showing that the approximate cation/anion stoichiometry is a function of the pH of the precipitation medium.

PRECIPITATE COUNTERION ANALYSIS

While the data obtained from infrared spectroscopy showed that the precipitates retained the initial ionic character of the interacting species, the question of the degree of association between the polyamine cationic and the color body anionic sites was not addressed. It was conceivable that some of the color body sites were located in such a manner that they were sterically unable to associate with polyamine cationic sites and vice versa. If this were the case, then a counterion would be withdrawn from the reaction medium in order to achieve localized electrical neutrality. This possibility was examined by determining sodium and chloride ion content of precipitates obtained from Fraction I at pH 7 using tetraethylenepentaamine and PEI 18 as the precipitants.

The sodium content was determined by digesting a sample of precipitate in perchloric acid followed by flame photometry. The results obtained are shown in Table X. In keeping with the format established in Tables VIII and IX, the data are shown as the milliequivalents of sodium ion normalized to 100% color removal from 1 liter of Fraction I.

In all cases, precipitate sodium content was low, less than 7% of the total ammonium ion contents shown in Table IX. However the sodium content of the PEI precipitates did appear to be higher than that for the tetraethylenepentaamine precipitates. Furthermore, the sodium content when color body was

in excess, i.e., when PEI 18 was limiting, appeared to be higher than when color removal was at its maximum.

TABLE X

THE SODIUM AND CHLORIDE CONTENT OF PRECIPITATES FROM POLYAMINE PRECIPITATION OF FRACTION I COLOR BODIES AT pH 7

	Polyamine, meq N/liter				
	Tetraethylenepentaamine		PEI 18		
	(4.0)	(12.0)	(2.3)	(2.7)	(3.0)
Percent color removal	89	91	28	99	98
Precipitate ammonium ion content (meq)[a,b]	--	0.99	--	1.11	--
Sodium content (meq)[a]	< 0.001	< 0.001	0.069	0.029	0.029
Chloride content (meq)[a]	0.016	0.035	0.024	0.064	0.075

[a] For 100% color removal from 1 liter of Fraction I.

[b] Assuming the ionic character of the polyamine in solution.

The determination of chloride ion content required a bit more sample preparation because the most widely used method, silver nitrate titration with potentiometric end-point determination (31) involved the use of aqueous solutions at acidic pH's. This presented a potential problem because, although precipitates could be resolubilized under alkaline conditions*, if the medium was then made acidic the color body-polyamine would reprecipitate. Other possible analytical techniques were explored without success. Thus the problem was approached by trying to separate the color bodies from the

* The precipitates from linear polyamines could be resolubilized by the addition of any base. Resolubilization of the PEI precipitates required pH control; thus to reconstitute in a small volume a buffered base was required, and ethylamine was quite adequate for this purpose.

chloride ions using gel permeation chromatography through Bio-Gel P-2, a polyacrylamide resin which excludes molecular weights of 1,600 and over. Initial work showed that over 97% of Fraction I total color could be found in the excluded fraction. Further study showed that chloride was completely included, that chloride could be determined in the presence of tetraethylene-pentaamine (see Materials, Equipment, and Experimental Procedures for details) and that chloride could be separated from PEI 18. These observations suggested that the method could provide an adequate estimate of the precipitate chloride content.

In the actual determinations, the precipitates were resolubilized in 0.5 to 1.0 ml by the addition of a few drops of a concentrated solution of ethylamine; a few drops of a 1.0M ethylamine-nitric acid pH 10 buffer was added, and then the concentrated solution was transferred to a P-2 column, previously equilibrated with 0.01M ethylamine-nitric acid buffer, pH 10. The sample was separated into two fractions, the excluded and included volumes, and then the chloride ion content fraction represented by the included volume was determined. The results are shown in Table X.

Precipitate chloride content was also low, <7% of the total ammonium ion equivalents shown in Table IX. If there was a trend, it was to have more chloride as the solution polyamine concentration increased; however this could be a reflection of the increased chloride concentration in the precipitation medium. Although little could be said about the way in which the sodium and chloride counterions came to be in the precipitate, the fact that the values were low indicated that both overall and localized electrical neutrality in the precipitate was achieved primarily through intimate association of color body anionic sites with polyamine cationic sites.

Thus the above results have shown that:

(1) Precipitation is related to the cationic character of the polyamine and the anionic character of the color bodies.

(2) The precipitate retained the carboxylate character of the color bodies.

(3) Overall electrical neutrality was achieved primarily by charge neutralization between polyamine cationic sites and color body anionic sites.

While these results enhanced the understanding of the system, they dealt only with the system after precipitation was completed; they did not clarify the sequence of events which led to precipitation. In an attempt to fill this void I followed the sequence of events in the early stages of precipitation by conductance measurements, and the later stages were investigated by determining the zeta potential of precipitating particles.

CHANGES IN RESISTIVITY DURING POLYAMINE-INITIATED COLOR BODY PRECIPITATION

Changes in resistivity during the precipitation of Fraction I color bodies by PEI 18 and tetraethylenepentaamine at pH 7 were studied. These amines were selected because PEI 18 was a rapid precipitant which was almost quantitatively removed at optimum color removal and showed a decrease in color removal when present in excess. In contrast, tetraethylenepentaamine was a slower precipitant that required the presence of nonprecipitating amine in order to achieve maximum color removal and was insensitive to the presence of excess polyamine.

When either PEI 18 or tetraethylenepentaamine at pH 7 was added to a pH 7 solution of Fraction I, the resistivity of the medium decreased (the conductivity increased) (Fig. 23). But, in both cases, the decrease in resistivity was significantly less than observed for the addition of either polyamine to a solution of KCl at the same pH and initial resistivity as the Fraction I solution. In contrast, the changes in resistivity due to the addition of ethylamine to Fraction I were indistinguishable from the changes observed for the addition of ethylamine to the KCl control. From these results, it was concluded that the polyamines complexed with Fraction I components, decreasing the number and/or effectiveness of the charge carrying species. In both cases the polyamine complexation was relatively rapid — it was completed in less than the 20 to 30 seconds required to obtain accurate resistivity measurements. Further, both polyamines complexed at polyamine concentrations which would not produce precipitation or even turbidity. From these data it was concluded that the different rates of color removal could not be attributed to grossly different rates of complexation in the initial phases of the precipitation.

The conductivity experiments also suggested that ethylamine did not interact with Fraction I color bodies. This interpretation was supported by the results from experiments studying the effects of ethylamine on color removal from Fraction I by ethylenediamine and diethylenetriamine (see Appendix V).

ZETA POTENTIAL MEASUREMENTS

The changes in the surface charge of Fraction I color body-polyamine precipitate particles as a function of polyamine concentration were examined by zeta potential measurements. The conditions chosen for study were

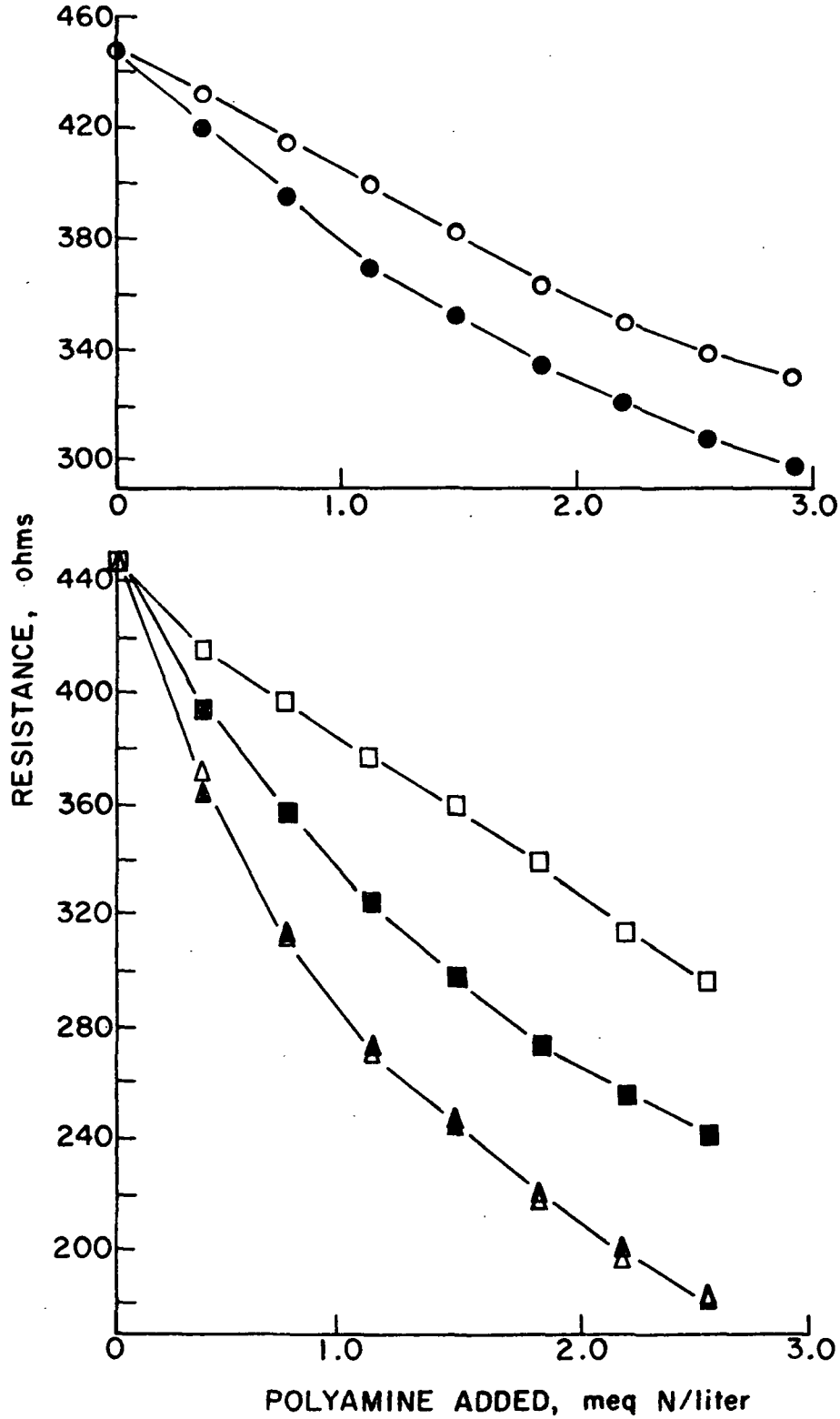


Figure 23. Resistivity as a Function of Polyamine Addition to pH 7 Solutions of Fraction I and Potassium Chloride

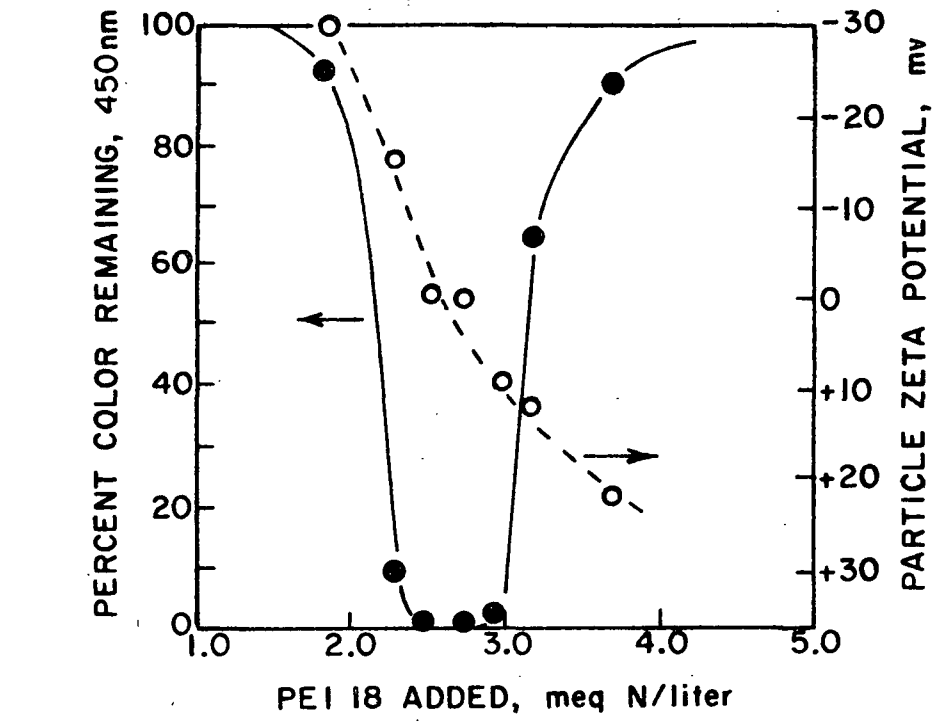
(o, ● PEI 18; □, ■ Tetraethylenepentaamine; Δ, ▲ Ethylamine; o, □, Δ amines added to Fraction I; ●, ■, ▲ amines added to KCl)

precipitation by PEI 18 and tetraethylenepentaamine at pH 7 for the same reasons as in the conductivity experiments. The results obtained are shown in Fig. 24.

When PEI 18 was added to Fraction I the particles formed on the descending portion of the color remaining curve showed negative zeta potentials, e.g., -30 mv at 90% color remaining. As the PEI 18 concentration was increased the zeta potentials observed became less negative and passed through zero at maximum color removal. On the ascending portion of the color remaining curve, where PEI 18 was present in excess, positive zeta potentials were observed and at 90% color remaining, particle zeta potential was about +22 mv.

With tetraethylenepentaamine the particles formed on the descending portion of the color remaining curve also showed negative zeta potentials. But, at maximum color removal, even in the presence of excess tetraethylenepentaamine, the zeta potentials remained slightly negative to zero. It was not possible to build up a positive zeta potential. Hence, the different color removal behavior with excesses of these two amines is accompanied by striking differences in the surface charge of the precipitating particles.

To test whether the zeta potentials observed with tetraethylenepentaamine were dependent upon the order of addition, another set of experiments was performed. In this series, the order of addition was reversed; Fraction I color bodies were added to solutions of tetraethylenepentaamine. In these experiments the ultimate color removal was about 90% and the zeta potentials observed were also slightly negative to zero, even when the tetraethylenepentaamine concentration was as high as 5.0 meq N/liter. Thus the order of addition had little effect on the ultimate color removal observed or the zeta potential of the precipitated particles.



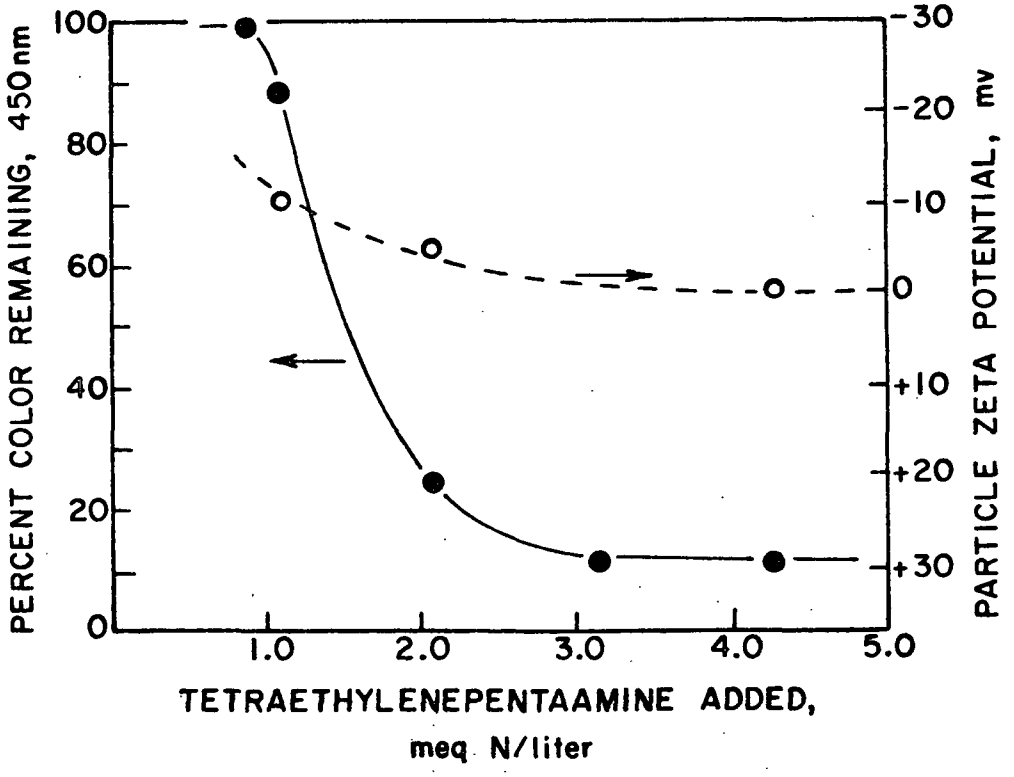


Figure 24. Zeta Potentials of Fraction I Particles Precipitated at pH 7

THE MECHANISM OF COLOR REMOVAL FROM FRACTION I

At the outset of the investigation it was hypothesized that precipitation proceeded via charge interactions between the anionic color bodies and the cationic polyamines. This hypothesis has been essentially substantiated by the results. Furthermore, the data are consistent with a general mechanism of precipitation. However, before beginning the discussion of the general mechanism, I want to point out that, in the precipitation, the particles pass through a colloidal state. When the particles are in this state, they are subject to factors which effect colloidal stability. Therefore, it would be worthwhile to review the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability (38).

DLVO THEORY

Basically the theory deals with colloidal systems which, when dispersed in an aqueous medium, develop a surface charge. As a result of the surface charge, counterions are drawn to the vicinity of the surface in order to maintain electrical neutrality. A portion of the counterions are closely associated with the surface of the particle. This dense immobile layer of counterions is referred to as the Stern layer (39). The remainder of the counterions are contained in a volume further removed from the surface of the particle than the Stern layer. This layer, which also contains ions having the same charge as the surface, is referred to as the Gouy layer (40). It is more diffuse than the Stern layer and comprises the other portion of the electrical double layer.

The effect of the double layer is to provide a charged sheath around the particle. The DLVO theory states that the net energy of interaction between two colloidal particles is the sum of their repulsive electrostatic

energy and their attractive Van der Waals energy. When two colloidal particles having the same charge approach each other, the double layers act as a barrier and prevent the particles from coming close enough to allow the Van der Waals attractive forces to exert an appreciable effect. When additional electrolyte is added, it reduces the extent of the double layer. This reduction or compression of the double layer allows particles on a collision course to become nearer before meeting resistance, and therefore the Van der Waals attractive forces exert a greater effect, enhancing the probability of agglomeration and precipitation. [For a more detailed development of the theory, see Verwey and Overbeek (41), or Kruyt (38).]

The forthcoming discussion will first present a general mechanism for color removal by the linear and branched polyamines. Then, the general mechanism will be extended to account for (1) color removal by the linear polyamines and for (2) color removal by the larger branched polyamines.

THE GENERAL MECHANISM

The first assumption in the general mechanism is that Fraction I color bodies, in solution, can be considered to be polyanionic species. This assumption is probably valid since titration showed that there are about 1.3 meqs of protonatable groups per liter of Fraction I (910 mg) at pH 7 (see Table IX), and gel permeation chromatography showed that some color bodies have apparent molecular weights as high as 10,000 (p. 35) and that most have apparent molecular weights over 1,600 (p. 62). If one assumes that an average color body has a molecular weight of 5,800, then this would be equivalent to a color body concentration of about 0.16 mM. Therefore the hypothetical average color body contains (1.3/0.16) or roughly 8 anionic sites per molecule at pH 7.

When the cationic polyamines are added to the anionic color bodies, a coulombic, attractive interaction leads to complex formation. The formation of the complex is rapid and can occur even at nonprecipitating polyamine concentrations, as shown by the conductivity experiments. The complexation results in a decrease in the anionic character and, as more polyamine is added, the size of the complex increases and aggregates form. The aggregates reflect the composition of the complexes and therefore still have a net negative charge. The addition of more polyamine promotes further aggregation, either by intimate association with a portion of the remaining anionic sites, i.e., direct charge neutralization, or by depressing the electrical double layer, thus enhancing the likelihood of aggregate association and subsequent precipitation, in accord with the DLVO theory of colloidal stability (38).

The precipitate retains the ionic character of the interacting species, that is, proton transfer to form uncharged functional groups does not appear to be significant if indeed it occurs at all (p. 60), and both localized and overall electrical neutrality is due primarily to the intimate association of the polyamine cationic sites with the color body anionic sites (p. 63).

This general mechanism is presumed to function in all cases; however the extent of complexation varies, depending upon the cationic character of the polyamine precipitant employed.

THE GENERAL MECHANISM WHEN LINEAR POLYAMINES ARE THE PRECIPITANTS

When the linear polyamines possessed two cationic sites, they only precipitated a portion of the color bodies, showing that the association of color bodies with these dications was limited. As the number of cationic

sites per polyamine molecule increased, the precipitation became more effective, and the concentration of amine required to achieve maximum color removal decreased. This enhanced precipitation may be attributed to the increased cationic character of the polyamine. This would be expected even if the same number of polyamine molecules were bound, since the cationic charge on a molar basis was greater, the resultant net charge on the complex would have to be less. However, it is possible that the polyamine possessing greater electrostatic repulsion between cationic sites may associate with color bodies more effectively. There is some evidence to support this speculation. Color removal increased with decreasing charge separation (p. 47). Hence, greater color removal was obtained when electrostatic repulsion within the diamine was greater. This speculation that complexation may provide a stabilizing influence for molecules possessing greater intramolecular electrostatic repulsion is supported by the potential energy relationships involved in the dissociation of an anion-cation pair. Since the energy level is proportional to intramolecular electrostatic repulsion, a dication with greater charge separation would dissociate more easily than a dication with less charge separation.

Zeta potential measurements showed that it was not possible to build up a positive surface charge when tetraethylenepentaamine was the precipitant, regardless of the order of addition (p. 67). If all color body anionic sites were equivalent, then positive zeta potentials should have been observed, therefore only a fraction of the color body anionic sites have a high affinity and accessibility for the polyamine.

THE GENERAL MECHANISM WHEN BRANCHED POLYAMINES ARE THE PRECIPITANTS

Color removal by the branched polyamines proceeds via the same general mechanism; however the branched polymers contain many more cationic sites per

molecule than the linear polyamines used. For instance, at pH 7, PEI 18 averages about 22 cationic sites versus 2.4 for tetraethylenepentaamine. Since only negatively charged particles were observed when color bodies were present in excess, several color body molecules must have interacted with each PEI 18 molecule. This situation would lead to much larger initial complexes than in the case of tetraethylenepentaamine, and, as more PEI 18 was added, the aggregates would form very quickly via a bridging mechanism. This would account for the more rapid rates of precipitation observed. When the concentration of PEI 18 was increased beyond that required for stoichiometric charge neutralization, the complexes and aggregates still formed but incorporated a greater portion of PEI 18 and thus had a net positive charge. As the PEI 18 concentration was further increased, the resultant electrostatic repulsion between aggregates prevented precipitation.

The mechanism just proposed attributed the rapid and quantitative precipitation by PEI 18 to the combined effects of high localized charge and polyamine size. This mechanism would predict that the stoichiometry observed in the precipitation of Fraction I color bodies with PEI 18 should be relatively insensitive to small dilutions. Figure 25 shows color removal by PEI 18 at pH 7 from Fraction I at three concentrations, one, one-half and one-quarter times the original Fraction I concentration.

When Fraction I was at its original concentation, 2.4 to 2.8 meq N/liter yielded maximum color removal. When Fraction I was at one-half the original concentration, maximum color removal was observed at PEI 18 concentrations of 1.3 to 1.5 meq N/liter. With Fraction I at one-quarter the original concentration, maximum color removal was observed at PEI 18 concentrations of 0.6 to 0.7 meq N/liter. Thus in accord with the proposed mechanism, the

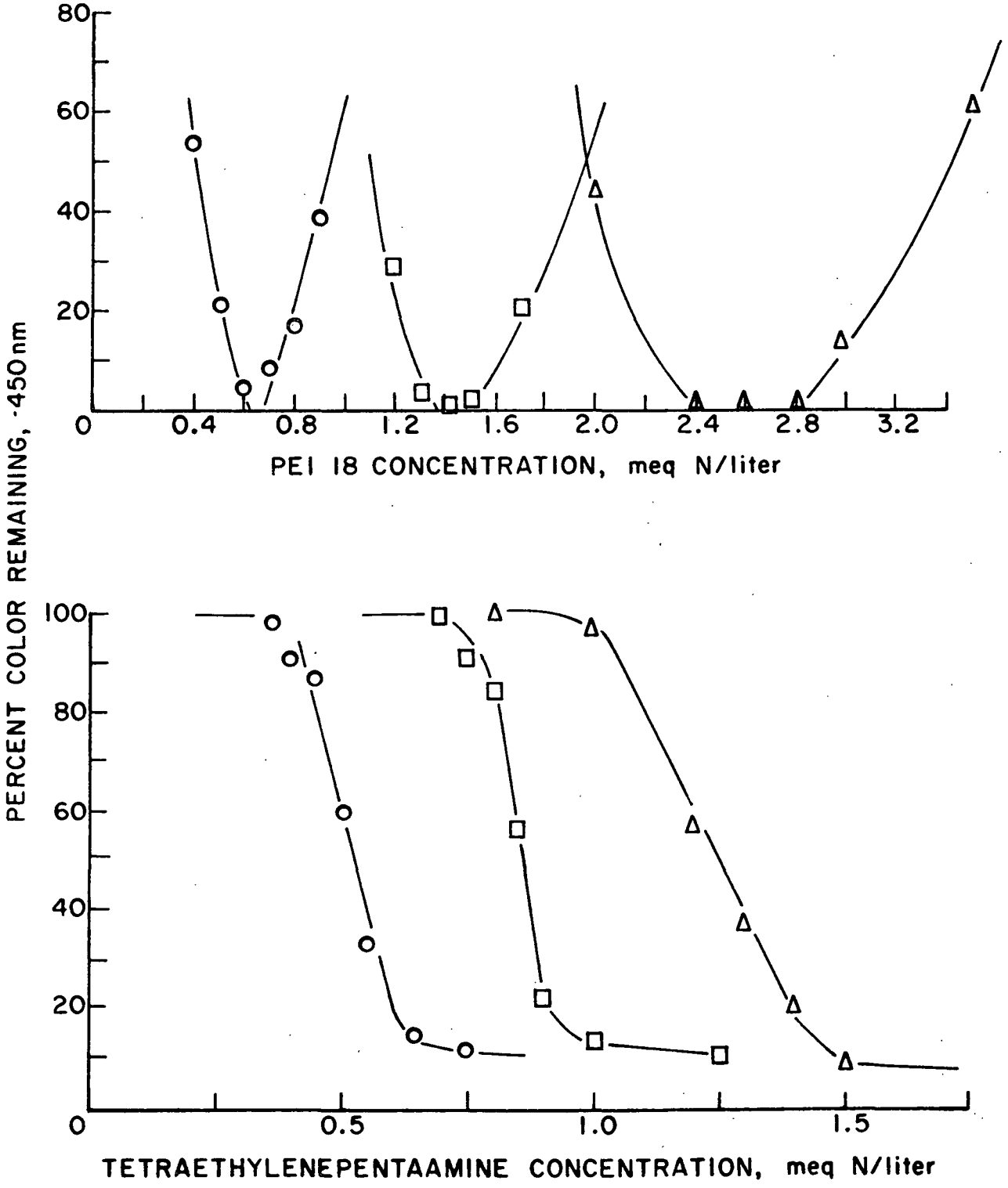


Figure 25. The Effect of Diluting Fraction I on Color Removal by PEI 18 at pH 7 and Tetraethylenepentaamine at pH 5. (Fraction I Concentrations: Δ = 1X, □ = 1/2X, o = 1/4X)

amount of PEI 18 required to achieve maximum color removal appeared to be directly proportional to the Fraction I concentration.

In the preceding discussion, a general mechanism was proposed and shown to be consistent with the data. However, the mechanism was general enough to be consistent with other more specific mechanisms. The forthcoming discussion will consider whether color removal from Fraction I can be attributed to solubility product (K_{sp}) phenomenon, to the destabilization of hydrophobic colloids by nonsorbable ions, or to the destabilization of hydrophilic colloids.

COLOR REMOVAL AS A POSSIBLE SOLUBILITY PRODUCT PHENOMENON

When the solid* phase of a sparingly soluble salt ($C_m A_n$) is in equilibrium with its ions in solution (C^{+x}, A^{-y}), the equilibrium constant for the reaction is given by

$$K = \frac{(a_{C^{+x}})^m (a_{A^{-y}})^n}{(a_{C_m A_n})}, \qquad (2)$$

where a is the activity of the species. However, since the activity of the solid phase is constant, the equilibrium can also be described by

$$K' = (a_{C^{+x}})^m (a_{A^{-y}})^n \qquad (3)$$

When the product of the activities of the interacting species in solution exceeds K', the K_{sp}, precipitation occurs (42).

*Although the solid phase is generally a crystalline solid, this is not always the case (48).

If color removal from Fraction I involved only K_{sp} considerations, then, at the point where precipitation begins, if the activity of one of the interacting species was decreased, the activity of the other species would have to be increased before precipitation would commence. Figure 25 also shows the effects of Fraction I dilution on color removal by tetraethylenepentaamine. As can be seen, the concentration of polyamine required to initiate precipitation decreased with Fraction I dilution. These data showed that color removal could not be explained as a simple K_{sp} phenomenon. The possibility that the change in reaction conditions, i.e., the dilution of Fraction I, could result in an increase in the activity coefficients of the interacting species, sufficient to explain the data, was considered unlikely.

COLOR REMOVAL AS A COLLOIDAL PHENOMENON

Another, more specific, mechanism which was considered involves the assumption that color bodies are colloidal species prior to the initial polyamine interaction. This argument would be based on the fact that a fraction of the color bodies were shown to have apparent molecular weights at least as high as 10,000 (p. 35), and consequently they would have diameters over 10 A, which by the definition of Ostwald (43), would classify them as colloidal species. This classification is arbitrary and not necessarily correct, but, for the sake of argument, let us assume that it is sufficient to classify the color bodies as colloidal particles.

Once this assumption has been made, the color bodies must then be subclassified as either hydrophobic colloids, hydrophilic colloids or some combination of the two.

If one assumes that color bodies are hydrophobic colloids, then the data are in agreement with the Schultz-Hardy rule (44), in that the

precipitation power of the polyamines was a function of the number of electrical charges they carried. Therefore precipitation might be explained as the destabilization of colloidal particles by nonsorbable ions. However, there is some evidence which would conflict with this theory. The evidence comes from the effects of ethylamine, sodium chloride, and calcium acetate on Fraction I color bodies at pH 7 (Table XI).

TABLE XI

THE EFFECTS OF MONO- AND DIVALENT CATIONS ON FRACTION I COLOR AT pH 7

Concentration, M	Color Remaining, %		
	Sodium Chloride	Ethylamine Hydrochloride	Calcium Acetate
0.002	--	--	104
0.004	--	--	108
0.006	--	--	99
0.008	--	--	51
0.010	100	100	37
0.020	--	--	30
0.040	--	--	31
0.060	--	--	30
0.080	--	--	31
0.100	100	100	30
0.200	--	--	30
0.500	100	100	28
1.000	100	100	--
1.500	99	100	--
2.000	100	99	--

At pH 7, neither ethylamine nor sodium chloride were able to show any appreciable color removal from Fraction I at concentrations as high as 2.0 molar. In contrast, when calcium acetate was added to Fraction I, precipitation occurred and a maximum color removal of 70% was obtained when calcium ion concentrations were 0.02M or more. If the calcium ion precipitation of Fraction I color bodies was to be regarded as the coagulation of hydrophobic colloids by nonsorbable ions, then in accord with the relationships established by Verwey and Overbeek (41), the effectiveness of the mono-, di-, and trivalent cations should be inversely proportional to the sixth power of

their valence, or molar ratios of roughly 100, 1.6, and 0.14, respectively. This would predict that a sodium ion concentration of 1.28M should produce an effect quite similar to a 0.02M calcium ion concentration. Since no color removal was observed at sodium or ethylammonium ion concentrations as high as 2.0M, color removal can not be attributed to the coagulation of hydrophobic colloids by nonsorbable ions.

Extending this argument to the trivalent cations, the Verwey-Overbeek (41) relationship predicts that if a divalent cation produced maximum coagulation at a concentration of 0.02M, then a trivalent cation should achieve similar color removal from Fraction I at a concentration of 1.75 mM. Yet Fig. 17 showed that 90% color removal from Fraction I at pH 7 was observed at tetraethylenepentaamine concentrations of 2.7 meq N/liter, or 0.55 mM, less than one-third the calculated value. Furthermore, at pH 7 tetraethylenepentaamine only has an average protonation of about 50% or 2.5 protonated sites per molecule.

Still another argument against a mechanism based strictly on DLVO theory can be presented by noting that color removal from Fraction I at pH 7 varied from 0% for ethylamine, to 50% for diethylenetriamine, to 90% for tetraethylenepentaamine. In the destabilization of a hydrophobic colloid, one would expect that the ultimate removal levels would be the same, the only difference being the cation concentration required to achieve that level of removal (45). Thus, it can be concluded reasonably that color removal from Fraction I by polyamines cannot be explained solely by the classical DLVO theory of the destabilization of hydrophobic colloids by nonsorbable ions.

The next question was whether the data could be explained if the color bodies were considered to be hydrophilic colloids. This facet of the

problem was approached as follows: In the coagulation of a hydrophilic colloid, the initial suppression of the electrical double layer would be as for the hydrophobic colloids. However, precipitation would not occur because of the interactions of the colloid with the medium, i.e., hydration or solvation. In these cases, the solvation shells must be dehydrated either by adding large excesses of electrolyte or by the addition of dehydrating agents such as anhydrous alcohols (46). Since it is difficult to imagine a system where 2.0M sodium chloride could have less "dehydrating capacity" than 0.02M calcium acetate or 0.55 mM tetraethylenepentaamine, the assumption that Fraction I color bodies could be regarded as hydrophilic colloids is considered unlikely.

Thus, the precipitation of Fraction I color bodies by polyamines cannot be fully explained by a classical solubility product phenomenon, by the destabilization of a hydrophobic colloid by nonsorbable ions, nor as the coagulation of a hydrophilic colloid. Therefore, the specific mechanism of precipitation must be something other than those considered or some combination of them.

Before attempting to extend the Fraction I mechanism to account for color removal from CES, it may be worthwhile to briefly review the observations and conclusions pertinent to the role of charge in color removal from Fraction I.

1. At a given pH the amount of polyamine precipitated is related to the cationic character of the polyamine (p. 57).
2. The ammonium ion equivalents of polyamine precipitated appear to be a function of the anionic character of Fraction I color bodies (p. 57).
3. The precipitate retains the carboxylate character of the color bodies (p. 60).

4. Precipitate electrical neutrality is achieved primarily by intimate association of anionic color body sites with cationic polyamine sites (p. 63).

5. Initial color body-polyamine interactions are rapid and occur even at nonprecipitating polyamine concentrations (p. 65).

6. The differences in the color removal curves for PEI 18 and tetraethylenepentaamine were accompanied by striking differences in the surface charge of the precipitating particles (p. 67).

The points just presented were used to formulate a general mechanism of precipitation. The mechanism involved a rapid initial coulombic attraction between the cationic polyamine and the anionic color bodies, which led to aggregate formation and precipitation.

THE MECHANISM OF COLOR REMOVAL FROM CES

There is some evidence to suggest that a sequence similar to that proposed for color removal from Fraction I can account for color removal from CES. The evidence is as follows:

1. The relative order of effectiveness and qualitative rates of precipitation for the various polyamines are similar in both color body systems.

2. Both systems show similar color removal profiles and enhanced precipitation when tricationic polyamine species are present.

3. The diethylenetriamine, pH 4, precipitates from CES and Fraction I show similar nitrogen contents, and color removal is proportional to precipitate dry weight. The same is true for tetraethylenepentaamine at pH 5 with both color body systems.

Since both color body systems showed similar behavior, similar mechanisms are probably operative.

While the above would suggest that the mechanism of color removal can be similar, some differences were observed. These include:

1. The polyamine content of Fraction I-PEI 18 precipitates is much lower than that found in the CES-PEI 18 precipitates. These differences are reflected in the lack of proportionality between color removal and precipitate dry weights.

2. With CES, the polyamines showed definite pH optima, whereas this was not found with Fraction I.

Presumably, a portion of these differences can be attributed to interactions with the soluble supernatant components which were not present in the acid-precipitated material (Fraction I).

MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

SOURCE AND PREPARATION OF CAUSTIC EXTRACT STANDARD (CES)

A 55 gallon, plastic lined drum of kraft, softwood caustic extract effluent was obtained from a nearby mill (Mill A), within 48 hours after sampling. During this period the drum was stored out-of-doors at ambient temperatures between 25 and 45°F. Upon receipt, the drum was turned on its side, rolled to insure mixing and a portion of the contents was transferred to several 5 gallon polyethylene containers. This material was then gravity filtered through Whatman No. 42 filter paper and filtered under nitrogen pressure through a 0.45 μm Millipore filter to remove suspended material. Very little material or color could be detected on the filters.

The filtrate was stored at 40°C for up to 25 days until it could be freeze-dried. After all the material had been freeze-dried, the powdery residue was pooled, thoroughly mixed, ground to a fine powder with mortar and pestle, and subjected to a vacuum of 35 μm of mercury for 27 hours. The reddish-brown powder (9.10 g/liter) was then parcelled into small polyethylene bottles which were tightly closed and stored over Drierite at -20°C until needed.

RECONSTITUTION OF CES

In all cases, the caustic extract standard (CES) was reconstituted just prior to use. A predetermined amount of CES (usually 0.455 g) was weighed into an appropriate vessel and then a volume of doubly distilled water, which was less than half that required for complete reconstitution (usually about 24 ml), was added with rapid stirring provided by a teflon-covered

magnetic stirring bar. The vessel was capped and stirred. The unused CES powder was then stored in a vacuum desiccator over Drierite until needed. After 15 to 20 minutes of stirring, the pH of the resolubilized CES solution was adjusted from 9.5 to the desired pH with 1.0M hydrochloric acid. Then, the volume was adjusted to exactly half that required for complete reconstitution (usually 25.0 ml) and the pH was readjusted if necessary. This 2X concentrate, 0.455 g/25 ml, was further diluted as required.

CHARACTERIZATION OF MILL A CAUSTIC EXTRACT AND CES

Solids (suspended, dissolved, total, volatile, and fixed), carbonate, chloride, turbidity*, and BOD_5* were determined by standard methods (31). Total organic carbon (TOC)* was measured with a Beckman carbonaceous analyzer. Sodium* and trace metal* contents were assayed by flame photometry. Calcium* was determined by emission spectroscopy and sedimentation coefficients* were measured using a Beckman Model E ultracentrifuge with schlieren optics. Conductivity was determined using an LKB Conductolyzer, Type 5300 B, and a platinum dip cell (1.0 cm). Absorption spectra of diluted CES, at the desired pH, were obtained using a Cary Model 15 recording spectrophotometer. Sugar contents* were determined by the method of Borchardt and Piper (32).

Titration curves were determined at room temperature using a Corning Model 7 pH meter (Corning Triple Purpose pH electrode versus a Calomel reference electrode), which was equipped with a Sargent recorder, Model MR. The titrant was added to a stirred solution of the material being titrated by means of a Technicon AutoAnalyzer proportioning pump. Flow rates were determined before and after titration and were consistent on a daily basis,

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*Performed by the Analytical Department, The Institute of Paper Chemistry.

generally about 0.6 ml/min. Solutions of doubly distilled water, at the volume and pH of the material being tested, were controls and were titrated under identical conditions.

SOURCE AND PREPARATION OF AMINES

Dow Chemical Company donated anhydrous samples of ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine, PEI 18, PEI 12, and PEI 6. The last three are branched polymers of ethylenimine, $\underline{M}_n$ 1,800 ± 300, 1,200 ± 150, and 600 ± 100, respectively.

The other mono- and diamines were purchased from Aldrich Chemical Company; all had stated purities of >99%.

Hexamethylethylenediammonium diiodide was synthesized by a modification of the method of Fuoss and Chu (33). One-half mole of N,N,N',N'-tetramethylethylenediamine was placed in a 1-liter beaker containing 500 ml of 95% methanol. A teflon covered stirring bar was added and the beaker was cooled in an ice bath. Then 141.0 g of methyl iodide (1.00 mole) was added slowly with stirring. After two hours the beaker was removed from the ice bath and allowed to stand at room temperature overnight. During this time the product crystallized. The crystals were broken up, collected by filtration, and washed with 100 ml of 95% ethanol. Then the crystals were dissolved in 100 ml of distilled water, 500 ml of 95% ethanol was added slowly with stirring, and the mixture was allowed to stand at 4°C for 1 week.

The large crystalline needles were collected by filtration and dried at room temperature for 48 hours. The dried crystals were parcelled into small aluminum foil-wrapped bottles and stored over Drierite until needed. The yield was 139 g (70.0%).

COLOR REMOVAL FROM CES BY POLYAMINES

To determine color removal, an aliquot of 2X concentrated CES, at the desired pH, was transferred to a 50-ml centrifuge tube which contained the desired amount of distilled water. The contents were mixed and then a predetermined volume of polyamine solution, at the desired pH, was added with mixing. In some cases, the pH was readjusted if required. In all cases, the final volume was such that CES was at its original concentration in the effluent (0.910 g/100 ml). The composition of samples for a typical experiment is shown in Table XII.

TABLE XII

COLOR REMOVAL FROM CES BY PEI 18;
SAMPLE MAKEUP FOR A TYPICAL EXPERIMENT

Tube Number	CES (2X, pH 7.0), ml	H_2O, ml	PEI 18 (5,000 ppm, pH 7.0), ml
a1	2.5	2.5	0.0
a2	2.5	2.4	0.1
a3	2.5	2.3	0.2
a4	2.5	2.2	0.3
.	.	.	.
.	.	.	.
ax	2.5	0.0	2.5

After all additions were made, the tubes were capped with parafilm and stored in the dark for 24 ± 1 hour. Then the samples were centrifuged at 12,000 g for 10 min and the 450 nm absorbance of the supernatant solutions was determined.

Samples with little or no color removal, such as Numbers a1 to a4 in Table XII, were diluted with distilled water prior to optical density determinations. Final pH's were checked and found to be within 0.2 pH unit of the initial. Data were expressed as percent of the original 450 nm absorbance at the pH in question (tube Number a1 in the above example). In some cases the precipitates obtained from centrifugation were washed with distilled water, freeze-dried, and their weights determined and recorded.

PREPARATION OF FRACTION I

Fraction I was prepared by slowly acidifying a 9X concentrated aqueous solution of CES (85 g/1040 ml) to pH 1 with concentrated hydrochloric acid. The acidified mixture was stored at 4°C for 20 hours. The precipitate which formed was collected by centrifugation (10,000 × g, 30 min), slurried with doubly distilled water, shell-frozen and freeze-dried. The powder obtained, which looked very much like freeze-dried coffee, was ground with mortar and pestle, parcelled into small containers, and stored in the dark over Drierite at -20°C. Yield: 8.5 g (10% of the initial CES weight).

The pH of the supernatant solution from centrifugation was raised to 5 by the addition of 25% sodium hydroxide, the volume was adjusted to 1,835 ml (to a concentration of 5X), and aliquots were frozen for future use.

RECONSTITUTION OF FRACTION I

Fraction I was reconstituted as described for CES (p. 82) except that the pH was adjusted to between 7 and 8 with 0.10M sodium hydroxide during the initial resolubilization. After dissolution, the pH was readjusted to that desired and the volume was adjusted to one-half that required for complete reconstitution. This 2X concentrate (0.091 g/50 ml) was further diluted as required.

COLOR REMOVAL FROM FRACTION I

Color removal from Fraction I was performed as described for CES (p. 85). However, in those cases with little or no color removal, optical density was determined directly (no dilution was required).

PRECIPITATE NITROGEN CONTENT

Precipitate nitrogen contents were determined using a Coleman Model 29 nitrogen analyzer, an automated instrument for rapid determination of total nitrogen by the micro-Dumas method (34,35). The Cuprin (metallic copper) and Cuprox (copper oxide) catalysts, and Causticon (KOH scrubbing solution) were purchased from Coleman. Matheson "Coleman grade carbon dioxide" was used throughout. The operating conditions were as follows: upper and lower furnace temperatures were 750°C, postcombustion furnace temperature was 550°C, CO_2 pressure was 4 to 5 psig, and CO_2 flow rates were 4.5 to 5.5 ml/sec.

Precipitate nitrogen content was calculated by determining the volume, in µl, of nitrogen gas produced and then applying appropriate correction factors for temperature, barometric pressure, etc. (35). Precipitate polyamine content was calculated assuming that all precipitate nitrogen was derived from the polyamine. During each series of determinations, at least one standard amine sample was included. The results for the known were within 0.2% of the theoretical nitrogen content.

SUPERNATANT POLYAMINE CONTENT

Some supernatant polyamine concentrations were determined by spectrophotometry using a modification of the method originally reported by Perrine and Landis (36) and later modified by Kindler (37) for PEI analysis. Appendix IV shows the development of the assay.

In its final form the procedure was as follows: An aliquot (between 0.5 and 2.0 ml) of supernatant solution obtained from a standard color removal determination (p. 85) was carefully pipeted into each of two 18 × 135 mm test tubes arbitrarily designated A and B. Each tube then received an aliquot of distilled water so that the final volume was 2.0 ml. The tubes were shaken and then 5.0 ml of 0.6M lead (plumbic) acetate at pH 5.3 was added with mixing. The lead acetate was prepared 18 to 24 hours in advance and filtered through Whatman No. 42 filter paper just prior to use. After 90 minutes, Tube A received 0.5 ml of freshly prepared 0.04M sodium acetate at pH 5.3, the solutions were mixed and the optical density at 290 nm was determined. Then, Tube B received 0.5 ml of freshly prepared 0.02M cupric acetate at pH 5.3, the solutions were mixed and the absorbance at 290 nm was determined. In all cases, the sample cuvette was rinsed with two ca. 1.5 ml aliquots of the sample in question before the absorbance was determined.

Supernatant polyamine concentration was determined from the difference (B-A) in absorbance, compared to a standard curve prepared with each series of determinations. Precipitate polyamine content was then determined by difference (polyamine added minus supernatant polyamine content determined).

INFRARED SPECTRA

Infrared spectra were obtained using a Perkin-Elmer Model 700 infrared spectrophotometer. For Fraction I and CES spectra, the color bodies were reconstituted, adjusted to the desired pH and freeze-dried. These freeze-dried powders were ground with KBr and pressed into pellets. The spectra of polyamine-initiated color body precipitates were obtained using freeze-dried precipitates collected by centrifugation.

PRECIPITATE COUNTERION CONTENTS

Precipitates for counterion analysis were obtained as described on p. 86) at pH 7, except that the final volume was 90 ml and duplicate samples were prepared. The precipitates were collected by centrifugation, washed with distilled water, freeze-dried, and their weights recorded. One set of samples was used to determine sodium ion content, using perchloric acid digestion followed by flame photometry. The other set was used to determine chloride ion content, using the following procedure: The precipitates were dissolved in 0.5 to 1.0 ml of distilled water by the addition of a few drops of 70% ethylamine in water. Then a few drops of 1.0M ethylamine whose pH had been adjusted to 10 by the addition of concentrated nitric acid was added and the concentrated color body solution was transferred to a Bio-Gel P-2 column having a total volume of 55 ml, which had been previously equilibrated with 0.01M ethylamine-nitric acid pH 10 buffer. The column was allowed to flow (0.7 ml/min), and the sample was separated into two fractions, the excluded and included volumes. The chloride content of the included volume was determined by potentiometry according to standard methods (31).

CONDUCTIVITY DETERMINATIONS

Conductivity (resistivity) was determined using an LKB Type 5300 B conductolyzer and a 1 cm platinum dip cell [cell constant: 0.1121 cm^{-1} (30°C)].

In a typical experiment, ten 0.5 ml aliquots of a concentrated (1600 ppm) solution of polyamine at pH 7 were added to 45 ml of a concentrated (0.0455 g/45 ml) solution of Fraction I at pH 7. The initial concentration of Fraction I was chosen so that after the additions were made, the final Fraction I concentration would be 1X. After each addition the solution was stirred and its temperature and pH were recorded. Then the dip cell was immersed and raised in the solution 8 to 10 times and the resistance of the solution was determined using the "flashing eye." In many cases the resistance was determined twice to check precision.

Two types of controls were performed in concert. In one type of control, polyamine was added to a pH 7 KCl solution whose conductivity had been adjusted to that of Fraction I. In the second, a Fraction I solution was taken through all the manipulations (i.e., stirring, temperature and pH determinations, conductivity determinations) without adding polyamine.

DETERMINATION OF ZETA POTENTIALS

Zeta potentials were determined using a Model B Zetameter (Zetameter Inc., New York, New York). In these experiments the standard color removal assay procedure was followed (p. 85) except, instead of centrifuging the sample, the suspended precipitate was transferred to the Zetameter cell. Zeta potentials were determined and then the samples were centrifuged and percent color removal determined. In those cases where few particles were suspended, a portion of the settled precipitate was resuspended in the supernatant solution by gentle agitation.

SUGGESTIONS FOR FUTURE RESEARCH

The present study has shown that polyamines can precipitate caustic extract color bodies and that precipitation was dependent upon the ionic character of the interacting species. It would be of fundamental interest to establish whether particular functional groups selectively participate in the complexation and, if so, what conditions favor their formation. This could be a part of an overall study of color body structure, and data gathered might then be used to determine the feasibility of modifying production conditions to yield color bodies which are easily removed or are less chromophoric.

This study also showed that, at optimum color removal, the percentage of polyamine found in the precipitate versus the solution concentration of polyamine increased as polyamine molecular weight increased. It would be of interest to the industry to determine whether polyamines of greater molecular weight could be quantitatively precipitated, recovered, and recycled. Experiments such as these would establish the feasibility of using polyamine decolorization of mill effluents. Along this line, similar experiments using chlorination stage effluent for pH adjustment should be attempted, as this could increase the percentage of total mill color removed and decrease operating costs.

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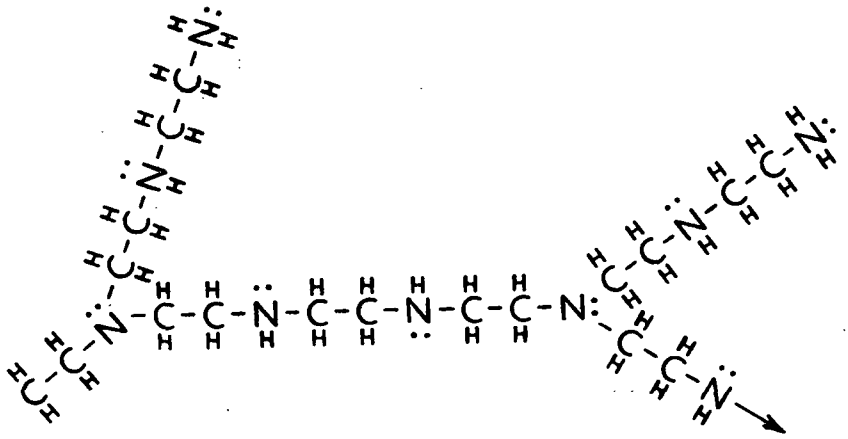
APPENDIX I

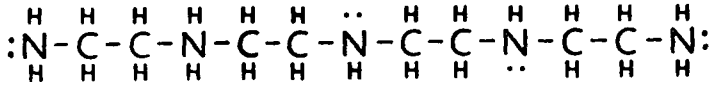
STRUCTURES OF THE POLYAMINES

A Typical PEI Segment

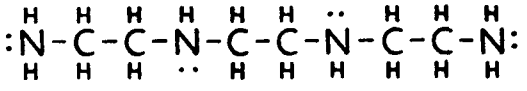


(The ratio of nitrogen is 1 primary:2 secondary:1 tertiary.)

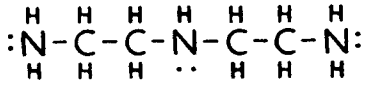
Tetraethylenepentaamine



Triethylenetetraamine



Diethylenetriamine



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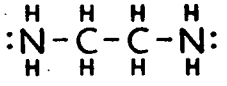
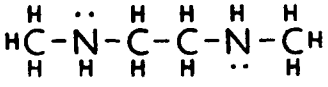


N,N'-Dimethylethylenediamine



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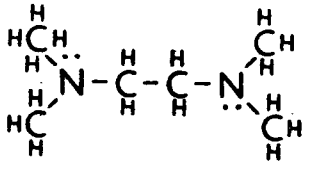
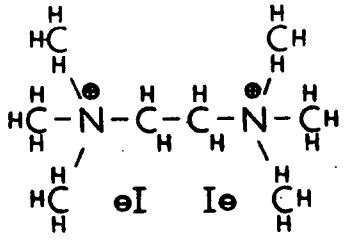
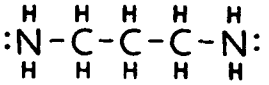


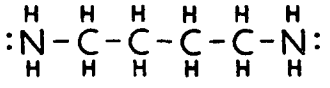
Hexamethylethylenediammonium Diiodide



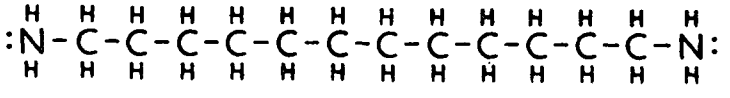
1,3-Diaminopropane



1,4-Diaminobutane



1,12-Diaminododecane



APPENDIX II

CES COLOR REMOVAL

TABLE XIII

COLOR REMOVAL FROM CES BY THE PEI SERIES[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm			
	pH 6	pH 7	pH 8	pH 9
PEI 18				
4.55	100	93.0	84.7	84.5
9.10	92.8	77.8	29.8	61.6
13.6	85.6	13.9	16.6	30.8
18.2	87.9	12.6	17.2	26.4
22.7	84.0	15.6	21.7	28.2
27.3	85.6	19.8	25.9	31.0
31.8	90.7	23.8	28.6	33.1
36.4	100	28.4	31.6	34.5
	pH 7	pH 7.5	pH 8.5	pH 9
PEI 12				
4.55	79.2	75.2	80.3	93.6
9.10	59.1	59.6	33.4	81.6
13.6	41.4	15.5	19.8	55.4
18.2	61.5	16.3	18.1	33.8
22.7	61.6	19.2	21.9	31.5
27.3	66.6	21.3	25.4	32.2
31.8	69.6	24.2	28.1	32.2
36.4	82.2	26.6	31.7	33.7
	pH 8	pH 8.5	pH 9	
PEI 6				
4.55	100	96.5	90.1	
9.10	67.1	69.4	71.6	
13.6	60.6	44.2	52.5	
18.2	68.5	31.7	35.5	
22.7	69.9	28.9	36.2	
27.3	72.2	30.1	34.5	
31.8	72.5	31.5	35.1	
36.4	81.6	32.2	35.3	

[a]Data are shown in Fig. 4.

TABLE XIV

COLOR REMOVAL FROM CES BY THE ETHYLENIMINE OLIGOMER SERIES[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm				
	pH 4	pH 5	pH 6	pH 7	
Tetraethylenepentaamine					
5.3	71.2	48.0	93.7	97.8	
10.6	68.6	37.2	60.6	87.2	
15.9	73.5	32.8	44.2	65.5	
21.2	73.5	31.5	38.3	56.5	
26.5	77.6	30.4	34.7	48.8	
31.8	81.6	30.8	33.8	47.5	
37.1	79.3	30.8	33.1	44.3	
42.4	82.4	32.1	32.9	42.6	
	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8
Triethylenetetraamine						
5.4	100	54.6	78.5	100	100	100
10.7	83.8	36.5	45.0	65.6	98.0	100
16.2	72.4	33.9	39.3	52.6	81.4	100
21.6	66.3	32.7	36.3	47.3	75.7	100
27.1	59.2	30.7	36.2	47.1	68.6	98.6
32.5	61.2	29.6	35.8	43.8	59.4	94.5
37.9	62.6	29.6	35.1	43.3	59.4	93.6
43.4	58.2	29.6	35.6	44.2	59.0	83.4
		pH 3	pH 4	pH 5	pH 5.5	
Diethylenetriamine						
5.8		77.5	91.4	100	100	
11.6		60.0	64.5	98.0	100	
17.5		56.5	57.0	79.4	97.6	
23.4		51.5	53.2	64.5	91.2	
29.2		50.4	50.1	58.6	91.2	
37.9		50.2	50.1	54.0	--	
46.7		50.4	50.0	53.9	73.9	

[a]Data are shown in Fig. 5.

TABLE XV

COLOR REMOVAL FROM CES BY DIAMINES[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm			
	pH 3	pH 4	pH 6	
Ethylenediamine				
200	85.6	87.5	90.8	
400	82.8	85.0	86.5	
600	82.7	84.3	86.4	
800	82.7	83.6	84.8	
1000	82.6	84.8	85.5	
	pH 4	pH 5.5	pH 7	pH 8.5
1,12-Diaminododecane				
10	--	41.1	27.6	28.5
16	34.1	--	--	--
20	--	28.5	20.5	20.7
30	--	25.8	17.8	18.9
32	29.8	--	--	--
40	--	24.5	16.5	18.1
48	28.7	--	--	--
50	--	23.8	16.4	17.7
60	--	23.6	17.1	17.6
64	26.8	--	--	--
70	--	23.3	16.5	17.4
80	26.2	23.3	16.8	16.9
100	--	23.1	16.7	15.5
112	25.9	--	--	--

[a]Data are shown in Fig. 6.

APPENDIX III

FRACTION I COLOR REMOVAL

TABLE XVI

COLOR REMOVAL FROM FRACTION I BY PEI 18[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm					
	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
0.23	68.4	--	--	--	--	--
0.45	53.2	67.6	--	--	--	--
0.68	37.4	63.4	--	--	--	--
0.91	2.5	47.3	74.4	97.0	100	98.5
1.14	0.8	26.8	--	--	--	--
1.36	35.7	2.2	48.2	--	--	--
1.59	--	67.6	30.1	--	--	--
1.82	66.7	--	3.4	55.6	88.5	98.5
2.05	--	44.7	3.1	--	--	--
2.27	79.2	--	12.0	--	--	--
2.73	--	72.3	36.6	0.2	1.4	37.6
3.18	95.2	--	--	--	--	--
4.09	100	89.5	61.4	--	--	--
4.54	--	--	--	87.0	1.8	0.2
11.4	--	--	--	100	100	80.7
22.8	--	--	--	--	100	95.5
45.4	--	--	--	--	--	100

[a]Data are shown in Fig. 15 and 16.

TABLE XVII

COLOR REMOVAL FROM FRACTION I BY PEI 12 AND 6[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm					
	PEI 12			PEI 6		
	pH 7	pH 8	pH 9	pH 7	pH 8	pH 9
1.14	74.3	95.0	93.4	84.4	94.0	100
2.28	1.7	9.0	93.4	2.7	59.4	85.8
4.54	--	--	--	3.4	4.5	5.3
6.82	91.5	53.6	6.4	5.0	4.8	5.9
13.6	--	--	--	7.2	7.2	8.5
18.2	100	98.6	14.3	--	--	--
27.2	100	100	16.9	--	--	--
34.0	--	--	--	8.4	10.2	11.8
40.9	100	100	19.7	--	--	--
57.0	100	100	21.6	9.5	12.2	14.3

[a]Data are shown in Fig. 17.

TABLE XVIII

COLOR REMOVAL FROM FRACTION I BY LINEAR POLYAMINES

Concentration, meq N/liter	Percent Color Remaining, 450 nm			
	pH 3	pH 5	pH 7	
Tetraethylenepentaamine[a]				
0.13	87.4	--	--	
0.26	73.4	--	--	
0.40	52.1	--	--	
0.53	23.3	--	--	
0.64	--	98.5	--	
0.66	7.6	--	--	
0.79	3.3	--	--	
0.85	--	96.5	--	
0.92	2.7	--	--	
1.06	2.6	83.5	100	
1.19	2.6	--	--	
1.27	--	14.2	--	
1.48	--	4.6	--	
1.59	--	--	100	
1.69	--	3.8	--	
1.88	--	4.0	--	
2.10	--	--	99.5	
2.38	--	4.0	73.4	
2.65	--	--	13.4	
2.98	--	--	9.5	
3.12	--	--	8.7	
	pH 3	pH 5	pH 6	pH 7
Diethylenetriamine[a]				
1.2	25.72	100	100	--
2.4	7.9	47.8	100	--
3.6	7.2	13.3	100	--
6.0	7.2	8.8	65.9	--
12.0	--	--	--	96.7
15.0	7.2	8.8	17.6	--
18.0	--	--	--	81.5
30.0	7.3	9.6	16.8	52.7
42.0	--	--	--	53.0
60.0	7.2	9.9	18.9	53.1

[a]Data are shown in Fig. 18.

TABLE XIX

COLOR REMOVAL FROM FRACTION I BY DIAMINES[a]

Concentration, meq N/liter	Percent Color Remaining, 450 nm			
	Ethylenediamine		N,N-Dimethylethylenediamine	
	pH 4	pH 6	pH 4	pH 6
10	93.0	98.7	95.1	99.1
20	44.8	80.3	58.3	93.3
40	33.2	73.7	39.2	89.6
60	30.6	69.6	38.6	87.4
100	30.1	68.4	38.8	86.7

	N,N,N,N-Tetramethylethylenediamine		Hexamethylethylenediammonium Diiodide	
	pH 4	pH 6	pH 4	pH 6
10	98.5	100	100	100
20	75.7	100	98.0	100
40	45.2	100	62.2	100
60	44.3	100	61.4	100
100	44.9	100	60.4	100

	Ethylenediamine	1,3-Diaminopropane	1,4-Diaminobutane
	pH 4	pH 4	pH 4
8	88.9	100	100
16	37.2	70.5	89.8
24	31.2	50.1	88.1
40	33.0	46.0	58.2
60	30.8	44.8	49.5
80	32.6	42.2	47.7
100	28.9	41.4	43.6

	1,12-Diaminododecane		
	pH 4	pH 6	pH 8
0.8	100	100	100
1.6	32.8	89.5	100
2.4	10.8	17.2	49.8
3.2	7.3	8.4	10.2
4.8	6.3	6.8	8.4
6.4	6.0	6.6	7.4
8.0	5.8	6.1	6.4
10.0	5.5	5.8	6.2

[a]Data are shown in Fig. 19-21.

APPENDIX IV

THE DEVELOPMENT OF A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF POLYAMINES IN THE PRESENCE OF CAUSTIC EXTRACT COLOR BODIES

When CES was found to have an appreciable nitrogen content it was desirable to determine precipitate polyamine content by some other method specific for the polyamine. The likely candidate was the spectrophotometric method recently used by Lindquist (29) to determine PEI concentrations. The procedure he used was as follows: A 5.0 ml sample of a solution containing 2 to 60 ppm PEI was added to 1.0 ml of 0.01M cupric acetate in 0.01M hydrochloric acid. The absorbance of the resultant solution was measured at 269 nm with a spectrophotometer zeroed with a blank containing 1.0 ml of the color reagent and 5.0 ml of the same solvent as the unknown PEI sample. The PEI concentration was determined by comparing the absorbance with a standard curve which obeyed Beers law. The complex formation between the PEI and cupric ion was pH sensitive and optimum results were achieved at pH's about 5.3.

The system described above was tried using dilute samples of CES and PEI 18. The results obtained were partially satisfactory in that when the 269 nm absorbance of the Cu-CES blank was subtracted from the absorbance of the Cu-CES-PEI 18 mixture the difference was in agreement with the PEI 18 standard curve. However there was a problem. When the absorbance of the Cu-water blank (line 2-1 in Fig. 26A) was added to the absorbance of the CES-water blank (line 4 in Fig. 26A) the sum was less than the absorbance of the Cu-CES-water blank (line 5 in Fig. 26A). Cupric ions were apparently complexing with CES components, increasing the absorptivity of the sample.* Therefore,

*Crozier (30) in an independent study, drew the same conclusion.

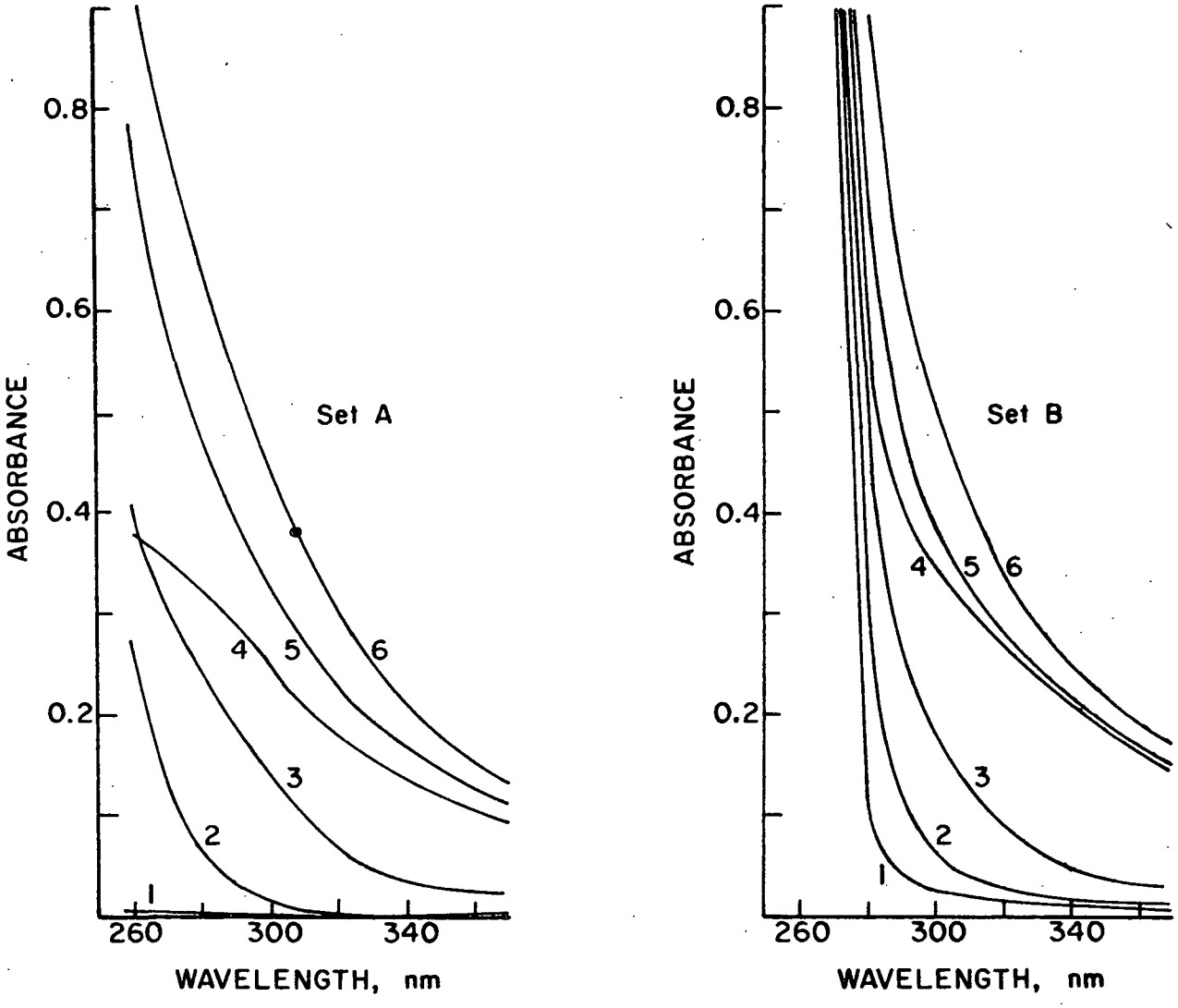


Figure 26. Spectra of PEI 18-Cupric Ion Complexes in the Presence of CES[a] and Lead (Plumbic) Acetate at pH 5.3

Set A: 1: 2.6 mM sodium acetate; 2: 1.3 mM cupric acetate; 3: 1.3 mM cupric acetate; PEI 18 30 ppm; 4: 2.6 mM sodium acetate, CES; 5: 1.3 mM cupric acetate, CES; 6: 1.3 mM cupric acetate, CES, PEI 18 30 ppm

Set B: Same as Set A except all samples are 0.5M lead acetate

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[a]CES at 0.12 mg/ml.

the system could only be applied if a suitable PEI-free blank was available. Although it was possible to assume that CES color bodies had uniform absorptivity when cupric ion was present and then just to dilute a CES sample to the appropriate color and consider this to be an acceptable blank, the assumption was considered unwarranted.

Since the dilution method was discarded, a possible solution to the problem was to disrupt, or prevent, the formation of the CES-Cu complexes. To this end a series of cupric ion sequestering agents was tested, without success. Having failed with this approach the problem was attacked from the opposite direction, CES was preincubated with a number of divalent metal cations and then cupric ion was added. These experiments showed that lead (plumbic) also interacted with CES. The reaction was such that the absorbance of a Pb-Cu solution (line 2-1 in Fig. 26B) plus the absorbance of a CES-Pb solution (line 4 in Fig. 26B) was equivalent to the absorbance of a Cu-Pb-CES solution (line 5 in Fig. 26B). The blanks were additive.

Although this observation was encouraging, it did not show that polyamine concentrations could be adequately estimated using this system. Thus the next step was to determine the validity of the assay system. However, from Fig. 26 it was evident that the combined effects of CES and lead acetate ruled out monitoring complex formation at 269 nm. Instead 290 nm was chosen as the reference wavelength.

Table XX gives the composition of several samples with varying CES and PEI 18 concentrations, and the PEI 18 concentrations determined using the procedure described on page 87 and the PEI 18 standard curve shown in Fig. 27.

TABLE XX

THE DETERMINATION OF PEI 18 CONCENTRATION IN THE PRESENCE OF CES USING THE CUPRIC-PLUMBIC ASSAY

Sample Number	Additions, ml			PEI 18 Concentration, ppm	
	PEI 18[a]	CES[b]	H_2O	Known	Determined
1	0.0	5.0	5.0	0.0	0.4
2	1.0	5.0	4.0	10.0	10.3
3	2.5	5.0	2.5	25.0	26.5
4	5.0	5.0	0.0	50.0	52.2
5	2.5	4.0	3.5	25.0	25.0
6	2.5	2.0	5.5	25.0	25.0

[a] 0.1 mg/ml, pH 7.

[b] 0.91 mg/ml, pH 7.

The results showed that the cupric-plumbic assay would provide a satisfactory estimate of the PEI 18 concentration in the presence of caustic extract color bodies. The next step in the development of the assay was to determine whether the method could be used to determine the concentration of other polyamines. Figure 27 also shows that although the extinction coefficient of the complexes decreases with decreasing molecular weight, the complexes still form, and their response was in accord with Beers law. Therefore, the procedure given in the Experimental section, based on the use of plumbic and cupric ion, was used for spectrophotometric determination of polyamines.

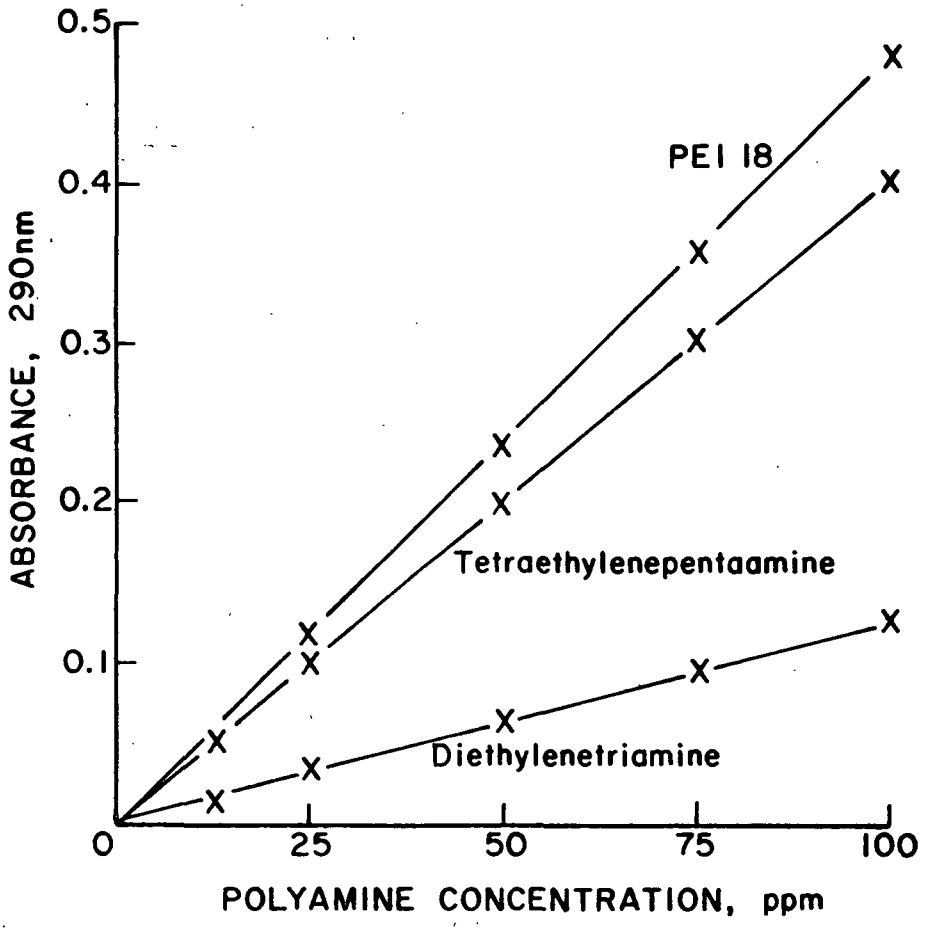

Figure 27. The Standard Curves of Several Polyamines Using the Cupric-Plumbic Assay System, pH 5.3

APPENDIX V

THE INHIBITION OF COLOR REMOVAL

Figure 28A shows the effects of including ethylamine or sodium chloride in the precipitation media on color removal from Fraction I by ethylenediamine at pH 4. When either of the two was present, the effect was to decrease the amount of color removal. Since the inhibition of color removal was equivalent for both ethylammonium and sodium cations, the effect must be attributed to the presence of cations in general, anions in general, or to their combined effect; increased ionic strength.

Figure 28B shows the effects of sodium chloride, ethylamine, and ethylenediamine on color removal from Fraction I by diethylenetriamine at pH 4. In contrast to the results obtained with ethylenediamine, the presence of 20 meqs of any of the three had little effect on the amount of color removal observed. As the concentration was increased beyond 20 meqs, inhibition was observed, but the inhibition was markedly less than observed with ethylenediamine. These data show that the diethylenetriamine-color body association is much stronger than the ethylenediamine-color body association. While these data are consistent with a mechanism involving the interaction of two oppositely charged ions, the unknown nature of the reactants and mechanism would make any attempt at further inference sheer speculation.

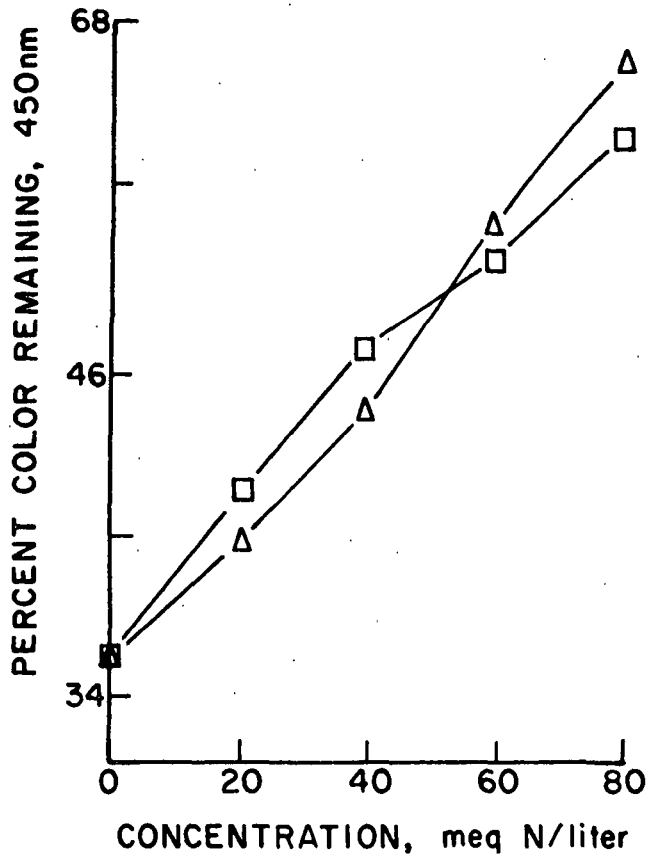

Figure 28A. The Effects of Sodium Chloride and Ethylamine on Color Removal from Fraction I by Ethylenediamine[a], pH 4

(Δ Ethylamine, □ Sodium Chloride)

[a]20 meq N/liter.

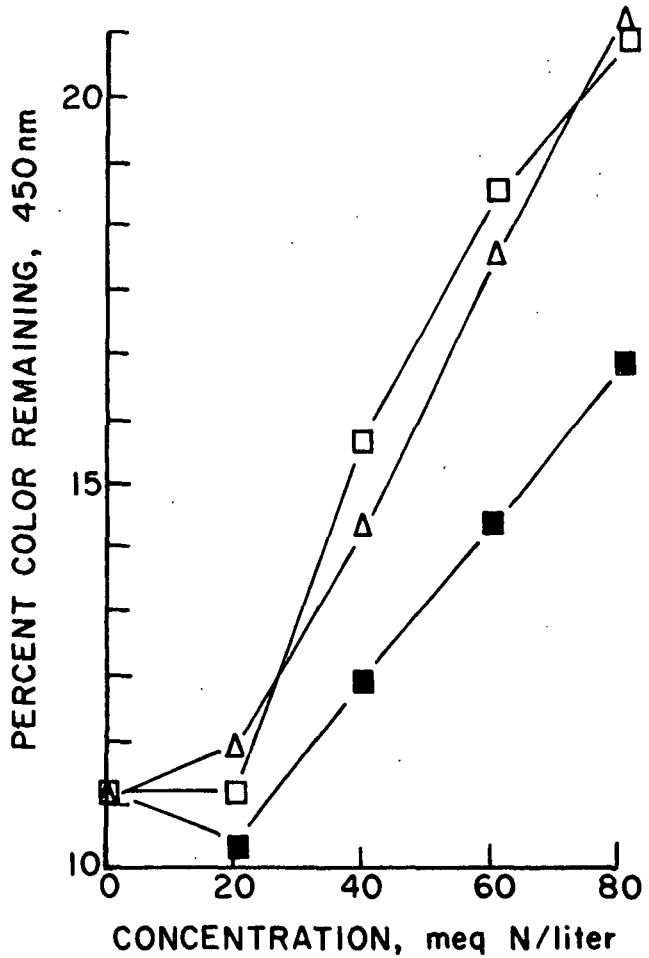

Figure 28B. The Effects of Sodium Chloride Ethylamine, and Ethylenediamine on Color Removal from Fraction I by Diethylenetriamine[a], pH 4

(Δ Ethylamine, □ Sodium Chloride, ■ Ethylenediamine)

[a]3.0 meq N/liter.